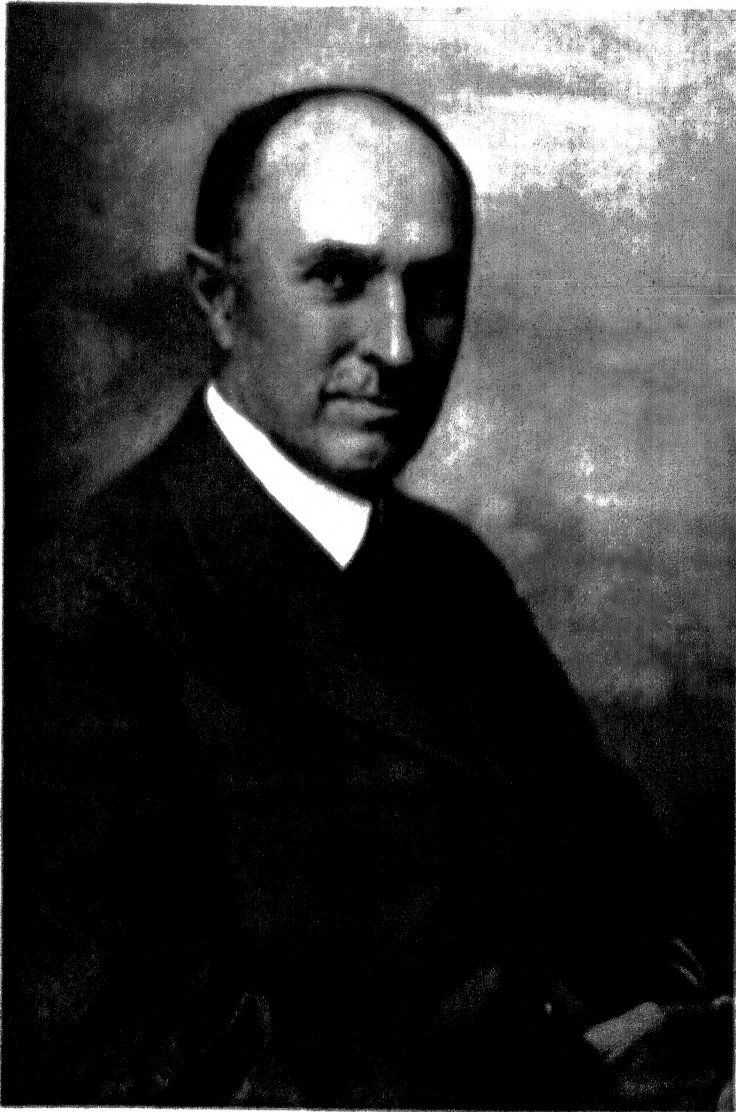


INDUSTRIAL MINERALS

AND ROCKS







**Seeley Wintersmith Mudd**

# INDUSTRIAL MINERALS AND ROCKS

(Nonmetallics Other than Fuels)

First Edition

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**T**O the title of this volume—Industrial Minerals and Rocks—is added a highly important subtitle: Nonmetallics Other than Fuels. As an alternative might be substituted the qualifying phrase "except metalliferous ores and mineral fuels." Native copper and petroleum, for instance, are industrial minerals, but they are not included in this book. Each of its forty-eight chapters deals either with a single or with a related group of those useful minerals or rocks commonly known as "nonmetallic." Of these no less than 70 are mined and used on a substantial scale. A calculation based on an estimate of the world's consumption, at average prices prevailing in the United States, indicates an annual production valued at between \$1,500,000,000 and \$2,000,000,000 at the mine. The United States alone accounts for more than half of the total; and the tonnage of such "ores" exceeds that of metalliferous ores, including iron, by a considerable margin.

Here is not only a large but a particularly fertile field for the engineer and technologist in the mineral industries. Only in recent years, and then only to a limited extent, have the search for, and the exploitation and beneficiation of, these minerals been conducted by men having professional engineering training. But more and more those who finance these operations are realizing the advantages of employing such men to manage and superintend their operations. The gradual exhaustion of surficial deposits and the consequent more elaborate mining methods; the need for mining ores of lower grade, resulting in the introduction of mechanical dressing and other types of processing; and the competition between materials, which demands that these things be done with the maximum efficiency—all these things require the highest possible skill, knowledge, and resourcefulness. The trend is distinctly toward the employment of technically educated men.

While many of the problems are essentially the same as those encountered in the metal and coal industries, there is enough of a special nature to warrant the introduction in "mineral industry" schools of sundry courses designed particularly for training in the nonmetallic industries. To assist undergraduate students and junior engineers to take advantage of the growing opportunity in this broad field is one of the purposes of this volume. And this is one of the considerations that moved the Seeley W. Mudd Memorial Fund Committee to sponsor it and recommend the appropriation from the Fund that made publication possible. Colonel Mudd was particularly mindful of the well-being of younger men in the



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INDUSTRIAL MINERALS

AND ROCKS



# INDUSTRIAL MINERALS AND ROCKS

## (NONMETALLICS OTHER THAN FUELS)

### CHAPTER I

### ABRASIVES

BY V. L. EARDLEY-WILMOT\*

**A**BRASIVES may be divided into two general classes, natural and manufactured. The former includes all rocks and minerals used for abrasive purposes without chemical or physical change, other than crushing, concentrating, shaping or bonding into suitable forms. Manufactured or artificial abrasives are made either by heat or chemical action from metals or raw mineral materials, and in recent years they have largely replaced natural abrasives, particularly for grinding metal.

Natural abrasives are found in many parts of the world. Roughly, the list includes all minerals capable of abrasive action, but the use of many of these as an abrasive is insignificant compared to their other uses. The principal natural abrasives in order of their hardness are diamond, corundum, emery, garnet, which are termed for convenience "high-grade natural abrasives," while "other natural abrasives" include mainly the various forms of silica, the chief of which is sandstone, which are listed separately under the heading of "Siliceous Abrasives."

Although abrasive materials are used in their natural, shaped or ground forms, they are mainly employed after fashioning into products such as grinding wheels and as abrasive-coated papers or cloths. Most of the wheels are made of manufactured abrasives, the quantity of emery and of corundum wheels being comparatively small. Grinding wheels are made by several processes, the products being known as: (1) vitrified, in which the bond is mainly clay; (2) silicate, having sodium silicate as the bond; (3) elastic, the bond being rubber; (4) those having Bakelite or artificial resin for the bond. Each form of wheel is made in many combinations, used for different kinds of grinding. In making the coated abrasive products, the sized grains of quartz, emery and garnet,

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or the manufactured silicon carbide and fused alumina, are automatically fed onto the moving glued backing of paper or cloth and after drying are covered with a thin coat of glue. The even distribution of the grain, both for "close coating" and "open coating," as well as the quality and temperature of the glue, are highly important factors requiring careful control. References to the methods of manufacture of these and other abrasive products will be found in the bibliography at the end of this chapter.

There is hardly an industry in which abrasives do not play some part, therefore the consumption of abrasives and abrasive products is largely dependent upon general business conditions. The automobile industry is the largest user, so that the total volume sales of abrasive somewhat closely precedes and parallels the fluctuations of the automobile output.

## HIGH-GRADE NATURAL ABRASIVES

### INDUSTRIAL DIAMONDS

Diamonds are reviewed in detail in chapter XVI, therefore only their uses as abrasive are outlined briefly below. There are two kinds of abrasive or industrial diamonds, the black diamond called "carbonado" or carbon, and "bort," the latter including badly colored, flawed or broken fragments of diamonds, unsuitable for gems, which are obtained principally from South Africa.

Carbons come mainly from the State of Bahia, Brazil. They are the toughest and hardest of all diamonds and are used nearly always in the crowns of diamond drills. The application of diamond drilling in the search for oil and ores (especially gold) has grown very much in recent years and the consumption of carbons has increased accordingly. An important use is for diamond dies in the wire-drawing industry, and another in the tools used for dressing and truing grinding wheels. Diamond-tipped tools are used for turning and boring substances such as hard rubber, vulcanite, Bakelite or hard metals, and in such industries as the electrical and automobile, which demand very accurate grinding work. Diamond-toothed saws are extensively used for cutting various kinds of stone. Composition diamond grinding wheels, introduced comparatively recently, are meeting with success.

Diamond dust is made by crushing diamonds in a special airtight steel mortar and then grading by the rates of settlement in olive oil. The prepared dust is used mainly for grinding or lapping diamonds and other gems, hard minerals, rocks, and cemented carbide products.

During the World War the uses for industrial diamonds, particularly in munition factories, developed considerably. It has been estimated that in recent years the consumption for abrasive purposes amounts to about 40 per cent in quantity and between 15 and 20 per cent in value of

the world's output of diamonds of all kinds.<sup>8</sup> During 1935 the stimulating effect caused by the increased demand for armaments and the desire to replenish diminished stocks led to a greatly increased consumption of industrial diamonds, which for some uses, such as tools for dressing wheels, amounted to almost 90 per cent.

### CORUNDUM

Corundum, an oxide of aluminum, is, next to the diamond, the hardest mineral known. Only within the last century has corundum, in the form of grain, been commercially used for abrasive purposes, though the natural crystals may have been used by the ancient Egyptians for carving hieroglyphics on their stone monuments. In ancient times the only known use for corundum was as jewels, ruby and sapphire being transparent forms of the finest corundum, though they were not recognized as forms of that mineral until 1805. Emery, on the other hand, a mixture of corundum and iron oxides, has been used as an abrasive for several centuries. A little over a century ago true corundum was recognized in the United States from samples found in South Carolina, but corundum mining did not start until 1871.

### COMPOSITION

Corundum is the sesquioxide of aluminum ( $\text{Al}_2\text{O}_3$ ) and has a theoretical composition of 52.9 per cent aluminum and 47.1 per cent oxygen, although invariably it contains small amounts of impurities such as silica, iron, lime and water. (See table of analyses of emery.) It is practically unaffected by even the strongest acids.

Corundum is generally classified in three groups: (1) gem stones, (2) common corundum, (3) emery. The gem stones include the transparent varieties recognized by name according to their color, thus the red is ruby, blue is sapphire and the yellow and green are sometimes erroneously called topaz and emerald. (The true topaz and emerald are really silicates of aluminum and beryllium.) Common corundum is opaque and varies in color and shades. It occurs as crystals—as "block" corundum, a massive form showing but little development of parting planes, or as "sand" corundum, minute crystals or small irregular grains sometimes found in ore bodies occurring on the contacts of schists and gneisses. Emery is described in detail later.

### PROPERTIES

*Color.*—Corundum shades from the deep blues and reds of the gems into opaque dull hues through white, gray, pink, bluish to brown or bronze, the browns and bronzes being the commonest. Often the shading of individual crystals changes from the center to the outside.

<sup>8</sup> References are at the end of the chapter.

*Hardness.*—The hardness is 9 on Mohs' scale. The various corundums differ in hardness, depending on the purity of the mineral, sapphire being the hardest.

*Crystal System.*—The system is a rhombohedral division of the hexagonal system, usually as long six-sided prisms that taper towards either end from the center, also short and stubby crystals assuming a barrel-shaped outline. The ends of the crystals are striated, forming equilateral triangles and the faces show distinct crosshatching. The common lamellar structure is due to twinning.

*Cleavage.*—Gem varieties break with a conchoidal fracture, but common corundum has a prominent basal parting causing crystals to break readily with smooth flat surfaces.

*Specific Gravity* varies from 4.10 to 3.93, depending on the amount of impurities present.

*Other Properties.*—Luster is adamantine to vitreous; sometimes pearly. It is transparent to almost opaque, depending on impurities present. It is very permeable to X-rays, which serves to distinguish the true gems from artificial stones as well as from minerals such as garnet or colored quartz. Pleochroism is very strong. The refractive index is high, but there is a low double refraction.

## ORIGIN AND MODE OF OCCURRENCE

Corundum is known to occur in about 20 kinds of rocks and in about 35 different countries throughout the world. The mineral is usually associated with peridotite in the United States, nepheline syenites in Canada and feldspathic rocks in India and South Africa. The origin of corundum has been discussed in some detail by several authors, among whom are A. E. Barlow,<sup>1</sup> J. H. Pratt,<sup>10</sup> A. L. Hall, T. H. Holland and others, a summary of each being given in the Mines Branch, Canada, report.<sup>3</sup> It appears generally accepted that corundum was one of the first constituents to crystallize out from the molten magma and, further, that in certain supersaturated aluminosilicate magmas the whole of the excess of the alumina separates out as corundum, provided that the iron, magnesia and silica present are low, but if these are high it separates out as spinel, cordierite and other minerals (ref. 2, p. 24). Corundum consequently does not occur in the immediate vicinity of free silica, such as quartz.

The South African corundum is invariably associated with pegmatite intrusions into basic rocks.<sup>4</sup>

## DISTRIBUTION OF DEPOSITS

Many of the occurrences of corundum are only of scientific interest. The countries having the main deposits of commercial importance

are the United States, Canada, Union of South Africa, India, Madagascar and Russia.

### *United States*

Corundum was first recognized in the United States a little over a century ago from a specimen submitted for identification from the Laurens district, South Carolina. Systematic mining for corundum, as distinguished from emery and the gem varieties, was first started at Corundum Hill, North Carolina.

The mineral has been found in many localities throughout the Appalachian belt from Massachusetts to Alabama, but only a few deposits have been developed. The best deposits are found in Jackson, Macon, and Clay Counties, North Carolina; and Rabun County, Georgia. Between 1900 and 1905 the corundum deposits of Gallatin County, Montana, were also worked to a small extent.

The Corundum Hill mine, Macon County, North Carolina, is about 8 miles northeast of Franklin on Cullasagee Creek, and is the largest corundum mine in the United States. The mineral occurs in a peridotite rock near its contact with gneiss. The deposit consists of a blunt lens-shaped mass of dunite, about 1200 ft. long and 450 ft. wide, and covers an area of about 10 acres. A number of veins of high-grade corundum rock in the dunite were worked by open cuts and tunnels, but with one exception they all pinched out. From the beginning of operations until 1900 the mine produced annually 200 to 300 tons of cleaned corundum. Several other mines in the immediate vicinity and in the same formation have also been worked for corundum between 1880 and 1890; these include the Behr mine, which had the best equipped corundum mill in the state; the Isbel mine, where the mineral occurs in an amphibolite dike, and the Herbert mine, where a number of very small veins of almost solid corundum occur in peridotite.

The most important Jackson County deposits are in the extreme northeastern part, in the vicinity of Sapphire, where there are numerous outcrops of peridotite in which the corundum is associated with garnet.

All the Georgia corundum deposits occur in lime-soda feldspar veins intersecting basic magnesian rocks of the peridotite type, usually on a contact with mica schist in close proximity to hornblende gneiss. Scattered occurrences are known in 13 counties, but the Lucas mine at Laurel Creek, Rabun County, is one of the best known corundum mines in the United States and was successfully operated between 1880 and 1893. Massive pieces of corundum weighing several hundreds of pounds were frequently encountered. The mineral occurs in an oval mass of altered peridotite about 2000 ft. long and 800 ft. wide, and is enclosed in a foliated quartz-mica gneiss.

Several hundred tons of corundum were mined prior to 1903 from the vicinity of Elk Creek in the central part of Gallatin County, Montana, where the ore occurs in syenites and pegmatites. A small production was obtained from York County, South Carolina.

### *World*

*Canada.*—Corundum was discovered in Canada in 1876 in Raglan Township, Renfrew County, Ontario. There are three recognized belts. The main belt of corundum-bearing nepheline syenites is approximately 103 miles long, with some interruptions, with a maximum width of 6 miles stretching through Renfrew, Hastings and Haliburton Counties, Ontario. The middle belt, in Peterborough County, 25 miles to the south, is a club-shaped area about 8 miles long and  $1\frac{1}{2}$  miles wide at the head. The southern belt, in Frontenac and Lanark Counties, 65 miles east of the middle belt, is about 12 miles long by 2 miles wide.

Prospecting has been carried out in about 50 different localities, but the principal operations were at Craigmont, in Raglan Township, at the Burgess mine, in Carlow County, and Jewellville mine, in Radcliffe Township, all in the main belt. A small tonnage was produced from Methuen Township in the middle belt. The Canadian mineral is brown to bronze, but an interesting deposit of blue corundum occurs on the York River in Dungannon Township.

Full details of the Canadian corundum deposits and operations are given in the Department of Mines reports.<sup>2</sup>

*Union of South Africa.*—Except for small quantities from Namaqualand and Rhodesia, the Transvaal has supplied the bulk of the corundum produced from South Africa since 1912, when the first shipments were made. The corundum-bearing areas cover 3000 sq. miles in the Zoutpansberg-Pietersburg-Leydsdorp districts of northeastern Transvaal. The ore occurs: (1) as primary deposits in altered feldspar, known as "boulder" corundum, (2) as secondary or eluvial deposits resulting from weathering of the softer rocks, leaving loose corundum concentrated to about 10 to 15 per cent of the volume, known as "crystal." The deposits are generally comparatively small, irregular in form, variable in corundum content and occur scattered over a very large area.

The rocks are feldspathic with dark mica as the principal accessory mineral, and are known locally as plumasites and marundites.

The recent bulletin issued by the Department of Mines of South Africa<sup>6</sup> gives full details of the deposits and operations.

*Southern Rhodesia.*—The principal deposits occur in eastern Mashonaland. About 2 miles southeast of Ruopapi, a number of corundum-bearing claims have been developed. The mineral is found in mica schist associated with granite, which underlies the corundum gravels. The

schist is decomposed to 60 ft., where crystals of an average size of  $1\frac{1}{2}$  in. occur. The annual output is very small.

*India.*—India is the home of the ruby and the sapphire, the principal ruby mines being about 100 miles north of Mandalay in Upper Burma. Corundum is widely scattered over Mysore State, and occurs in pegmatites, diorites, basalts, etc. In recent years operations have been confined to the Salem district of Madras, while previous to 1920 a small output was maintained from near Pipra, in Rewah State. There is still, and for many generations has been, a certain trade in Indian corundum used by the old armorer and lapidary, and even today the material is a regular item of trade in the bazaar cities of Delhi, Agra and Jaipur, where the lapidary still flourishes.

There does not appear to be any regular mining of the mineral but it is collected in a casual way by agriculturalists and cowherds who dispose of it through agents to the larger dealer in the big cities.

Details of the annual production from various districts are given in the records of the Geological Survey of India.<sup>3</sup>

*Madagascar.*—Corundum occurs in a soft, decomposed siliceous rock, which forms the so-called "red earth" that covers a large part of the surface of the island; sometimes to a depth of 60 ft. In places this earth has been washed from the summits and sides of hills, leaving the heavy minerals such as corundum, which are concentrated at the bottoms. Typical deposits occur in the southwest of Ambositra; also at Maovatanana and Betafo. The mineral is usually opaque and bluish in color, showing mica incrustations. Production has been steady since 1910, dwindling from a maximum of 800 tons in 1919 to 9 tons in 1931. Mining operations were renewed towards the end of 1935, when 12 tons was exported and production was maintained on a comparatively large scale in 1936.

*Soviet Russia.*—Small lenses of coarse-grained corundum occur in the western part of the Ilmen Mountains near the town of Kyshtym. The deposits were worked during the World War and considerable tonnage of the mineral has been mined in recent years from near Lake Tscherkakul, in the Bajan-Aul division of the Pavlodar district.

## COMMERCIAL CONTROL

In spite of the severe competition from manufactured abrasives, particularly fused alumina, or artificial corundum, the output from South Africa in 1935 almost equaled the record of 1926, and the imports into the United States were also the highest since that year. The cheapness and comparative ease with which the South African crystals are obtained by washing the eluvial gravels bars competition from the United States, Canada, and other countries in which the mineral is mined from the solid rock and must undergo crushing and concentration at considerable



expense. The bulk of the South African crystal corundum is shipped to one or two grinders in the United States, where it is crushed and graded for the market.

Any large consumption of corundum in the future is unlikely because of the development of manufactured abrasives, with their highly controlled products, their ability to duplicate requirements exactly and consistently and their constant improvements and the expansion of their application. The extent of this all-round control is impossible with the natural mineral.

The maintenance of the market for South African corundum in the face of the competition from manufactured abrasive is due to its special suitability for certain uses, comparative cheapness and in recent years, to the existence of efficient channels for its distribution in the United States, and to the fact that the grading of all corundum for export now comes under government control. Prior to the improvement of the grading and export regulations, some manufacturers, both in Europe and in the United States, had unfortunate experiences with regard to the quality and regularity of shipments. Efforts to gain the European market have failed, owing to lack of a proper distribution and selling organization as well as to loss in confidence from past irregular shipments, but early in 1936 an increased demand for corundum came from England.

h.

### PRODUCTION AND CONSUMPTION

Recorded statistics of true corundum production with the exception of Canada and South Africa are either intermittent or unobtainable.

#### *World*

*United States.*—Mining of corundum first started in North Carolina in 1871. Except for a little activity during the World War, there has been no production since 1905. This was first due to the keen competition from Canada, which started a little prior to that year, and since the beginning of the war, from South Africa. Apart from these sources of the natural mineral, the United States and Canada are the leading producers of highly efficient manufactured abrasives, a fact that does not encourage the production of natural corundum.

United States statistics group corundum and emery together, so that the true corundum output is not recorded except between 1894 and 1900, when separate records showed a total of 3720 tons of corundum.

*Canada.*—During the period 1900 to 1921, Canada was a regular and for many years the world's leading producer of true corundum. The peak was reached in 1906 and 1907, when 2500 and 3000 tons of graded grain were sold. During the last three years of production, the corundum was obtained as concentrate from treating the old tailing dumps. The total output during the 21 years amounted to 20,422 tons of graded grain



valued at \$2,104,251. There has been no production since 1921 other than an occasional shipment.

*Union of South Africa.*—Production has been steady since 1912, that of the peak year in 1926 being 5996 short tons and the next largest 4851 tons in 1936. The total shipments to date amount to 47,423 short tons valued at £341,420. At least 90 per cent of this has been in the form of crystal derived from eluvial deposits, recovered mainly by primitive methods. Owing, however, to the depletion of the known eluvial, more attention is now being paid to reef deposits and probably about half the present product is derived from reefs and in the future the proportion is likely to be even higher. The Union production since 1920 has been as follows:

YEAR	LONG TONS	YEAR	LONG TONS
1920	243	1928	1791
1921	110	1929	3220
1922	2035	1930	2275
1923	2928	1931	1008
1924	1288	1932	323
1925	1740	1933	1164
1926	5388	1934	2859
1927	917	1935	4264
		1936	4322

*Other Countries.*—Southern Rhodesian production from 1924 to 1930 was 37, 43, 39, nil, 22, 19 and in 1930 it was 10 long tons. Since then the output has ceased. Namaqualand produced 13 tons in 1920; 10 tons in 1923 and none since. India in 1920 and 1921 recorded 210 tons in 1920 and 64 tons in 1921 and from 1925 to 1930 it has produced 10, 28, 65, 21, 34 and 30 long tons, by years. Madagascar's output from 1920 to 1931 was as follows: 513, 280, 183, 411, 145, 222, 115, 150, 113, 113, nil and 1. The substantial output from Soviet Russia may include emery, which is also produced from the same region as that of corundum. The figures given by the Imperial Institute (London) Statistical Summary for Russia for 1924 to 1928 are 1409, 709, 884, 2636, and 6876 long tons.

#### MINING METHODS AND PREPARATION FOR MARKET

In most instances ordinary open-cast methods are employed in mining corundum. In the Transvaal most of the mineral is obtained by individual farmers or diggers, it being estimated that during the first half of 1935 over 300 Europeans and about 4000 natives were engaged in digging corundum. The openings are shallow, very few being as deep as 20 ft. At the deeper workings, which are down about 100 ft., as at Blinkwater, Borkum and Westphalia, the broken rock is hoisted by means of hand-operated or power-driven cranes, or shoveled up by stages from one platform to another.

In the eluvial deposits of the Transvaal, where the corundum is clean and generally free from adhering impurities, the material is first passed

over rocking inclined screens of about 1-in. mesh and thence over  $\frac{1}{8}$ -in. screens. The minus 1 plus  $\frac{1}{8}$ -in. material is washed in rotary pans and then hand-gravitated or jigged on small circular hand sieves. The large corundum crystals are picked out during the coarse-screening operations. The cleaned corundum is collected, sun-dried and graded into three sizes, as laid down in the Export and Grading Regulations, the final grading being done at the various buyers' depots. Boulder corundum, being in a massive form, is merely broken up by blasting and sledge hammers into fragments small enough to be handled for sale and export.

In the reef corundum or primary deposits, mining has been confined mainly to the friable and weathered plumasites or micaceous gneisses in which the corundum crystals break away with but little adhering gangue. The mineral is extracted first by hand-cobbing and the residue is cleaned by revolving in specially fitted cylindrical metal drums whereby the soft gangue is knocked off the crystals. At the Geber deposit at Blinkwater, which at present is the largest and most consistent producer in northern Transvaal, a better type of mill is used. The plus  $\frac{1}{8}$ -in. material is revolved at a high speed in a 10-ft. by 18-in. steel pipe through which a shaft with numerous beater blades is fitted, operated either wet or dry. It is more drastic and quicker than the barrel or other types. Grain corundum and concentrate are being produced by the Transvaal Corundum Co. near Bandolier Kop from the hard reef deposits. Ordinary wet gravity methods of crushing, stamping, jigging and tabling are employed. A flowsheet of this plant and much detail as to the treatment of South African corundum is given in the recent bulletin by W. Kupferburger.<sup>6</sup> References to treatment plants in Canada and the United States will be found in the bibliography at the end of the chapter.

The crude South African crystal corundum exported to the United States is ground, screened and graded into sizes required by the market. The sizes of the grain range from 6 to 200 mesh by screening and to F, or flour, grades by means of air and water classification.

#### SPECIFICATIONS, MARKETING, USES AND PRICES

*Specifications.*—For abrasive purposes corundum should have a bright and glassy luster and not be dull; the broken grain should be angular, uneven and sharp, not smooth or even; cleavage or parting planes should be absent, or nearly so; there should be no inclusions of other minerals; as a general rule the large corundum crystals are better than the very small ones.

*Marketing.*—The South African corundum is mainly collected by diggers and brought to central distribution agents. The Gifter Corundum Co. has recently erected large buildings for the treatment of corundum and has also established a depot in the heart of the corundum fields, so that diggers will be able to effect delivery within a few miles of the

producing sites. No corundum is exported without being certified by the government grading organization as up to the standards and specifications given in the Restricted Minerals Export Act No. 35 of 1927. Grade A is over 92 per cent  $\text{Al}_2\text{O}_3$ ; B is 90 to 92 per cent; C is 85 to 90 per cent and D is under 82 per cent  $\text{Al}_2\text{O}_3$ . Full details are given in the *South African Bulletin*,<sup>6</sup> and in the *South African Mining and Engineering Journal*.<sup>4</sup>

*Uses.*—The chief uses for corundum are as gem stones and abrasives. Gem, or precious, corundum is covered in chapter XVI.

The corundum of fine and flour grades is used as a loose grain for polishing rock specimens, gem polishing and for glass grinding and beveling, the largest consumption being in the latter trade, particularly for grinding lenses. At one time, before the introduction of manufactured abrasives, corundum was extensively used for "sand" papers but on the American continent is no longer employed for that purpose. The graded grain is mixed with bonds and made into grinding wheels, mainly by the vitrifying process. For certain purposes, some users prefer corundum to the manufactured abrasive wheels. About 70 per cent of the corundum used in the United States is made into grinding wheels and about 20 per cent goes to the glass and polishing trades.

In the United States a few hundred tons of South African corundum are used instead of bauxite for an alumina abrasive specially fused in the electric furnace. Before the expiration of the patent in which pure white alumina is used as the ingredient, appreciably more corundum was employed, but at present only one firm, owning the corundum patent, uses the natural mineral as the ingredient of a special alumina abrasive.

*Prices.*—The production value within South Africa for 1935 for boulder corundum was \$18.30; crystal, \$37.50 and concentrate, \$59 per short ton, whereas the import value of crude crystals in the United States was \$61 per short ton.

## EMERY

Emery is an intimate mixture of granular corundum and magnetite with some hematite. It takes its name from Cape Emeri, on the island of Naxos, in the Grecian archipelago, where it occurs in great abundance and from which it has been mined for several centuries.

## COMPOSITION

Mineralogically, emery is divided into three varieties: (1) true emery (2) spinel emery, (3) feldspathic emery. It is regarded as a mechanical admixture.

True emery is a mixture of corundum and magnetite, with or without hematite derived from the magnetite, such as the Greek and Turkish emery, and is usually of a reddish black tint.

Spinel emery is a mixture of spinel (pleonastehercynite) corundum and magnetite, the corundum being present in variable proportions and sometimes entirely lacking. It is usually a heavy, black, fine-grained aggregate with dark gray crystals of corundum appearing in the best varieties. The crystals often are cracked and considerably altered to hydrous mica. This kind is mined in New York and Virginia in the United States.

Feldspathic emery is similar to the spinel but contains in addition from 30 to 50 per cent plagioclase. Pure magnetite often is found in streaks within this mass.

There are at least three recognized grades of emery: Greek or Naxos, Turkish and American. Each one varies as to its chemical and physical properties.

TABLE 1.—*Analyses of Emery from Different Localities*

Locality	Alumina	Silica	Magnetic Iron Oxide	Lime	Magnesia	Water	Total
<b>Greece:</b>							
Naxos.....	62.64	4.90	31.41	0.45	0.06	1.04	100.50
Naxos.....	68.53	3.10	24.10	0.86		4.72	101.31
Naxos.....	57.69	6.36	30.87	0.89	0.20	3.99	100.00
Nicaria.....	75.12	6.88	13.06	0.72		3.10	98.88
<b>Turkey:</b>							
Kulah.....	63.50	1.61	33.25	0.92		1.90	101.18
Gumuch.....	60.10	1.80	33.20	0.48		5.62	101.20
Samos.....	70.10 <sup>a</sup>	4.00	22.21	0.62		2.10	99.03
<b>U. S. A.:</b>							
Virginia.....	45.38	2.53	41.23	0.06	5.71	1.32	96.23
Chester, Mass..	50.02	3.25	44.11			n.d.	97.36
New York.....	59.22 <sup>b</sup>	0.84	30.68		3.54	2.70	96.98
New York.....	50.10	14.32	28.17	0.84	4.31	n.d.	97.74

<sup>a</sup> Also contains 3.72 per cent  $\text{TiO}_2$  (ilmenite) and some of the alumina as spinel.

<sup>b</sup> Also contains 3.28 per cent  $\text{TiO}_2$  (ilmenite) and some of the alumina as spinel.

### PROPERTIES

Emery is a massive, nearly opaque, dark gray to blue-black, sometimes mottled, mineral. Its specific gravity varies from 2.7 to 4.3; it has a hardness of about 8, breaks with a moderately regular fracture, and is always more or less magnetic. The appearance, hardness, composition and color vary according to the locality in which it occurs. The hardness depends upon the amount of corundum contained and the emery may be either fine grained or coarse grained, depending on the size of the corundum crystals present.

### ORIGIN AND MODE OF OCCURRENCE

Emery usually occurs in crystalline limestones and schists, also in peridotite and diorite. It is often associated with chlorite in hornblende

schists. Further details of the mode of occurrence are given in the description of world deposits.<sup>2,4,7,8</sup>

## DISTRIBUTION OF DEPOSITS

### *United States*

Emery is known to occur at a number of places in the eastern United States, but has been mined only from Chester, Mass.; Peekskill district, New York, and Whittles, Virginia.

*Massachusetts.*—Emery was discovered in Hampden County, at South Mountain, near Chester, in 1864 by Dr. H. S. Lucas, although 30 years previously the deposit had been unsuccessfully worked as an iron mine. Previous to 1913, practically all the emery from the United States was produced from this locality. The deposits are associated with a narrow band of amphibolite that extends almost continuously across the state. In the vicinity of Chester this band is about  $\frac{3}{4}$  mile wide, and the emery deposits can be traced for about 5 miles. The deposits occur in the form of a vein in the eastern side of the band, in close proximity to sericite schist. The emery is found in pockets from a few feet to 12 ft. wide and has been mined in places to a depth of 300 ft. Six or seven mines were operated along this vein and large quantities of ore were extracted, but the workings have been abandoned since 1913.

*Virginia.*—A spinel emery occurs to the west and south of Whittles, Pittsylvania County. Although the deposits were exploited many years ago for iron ore, they were not successfully worked for an abrasive until 1917 and for the next 11 years yielded a large quantity of good material.

There are two types of occurrence: (1) schist ores, in which thin bands of quartzite, interbedded with the schists in places, form one, and sometimes both, walls of the emery bodies; the rock being closely jointed and in many places pegmatitic; (2) granite ores, or those enclosed in a decayed granite, which often is cut by narrow, pegmatite dikes. The emery in both types is a heavy, black, fine-grained crystalline aggregate. Weathering has progressed to an advanced stage, so that in all the ore deposits the rocks are entirely decomposed, and owing to alteration of the schists into varicolored mottled clays, the surfaces of the emery bodies are often coated with a deep red clay. The ore bodies occur as irregularly shaped lenticular masses of solid emery, the largest of which is about 130 ft. long and 6 to 8 ft. wide.

The method of mining was based on the strongly developed joint structure of the emery bodies. After the decomposed rocks were removed, the emery blocks were dislodged by forcing iron bars into the joints. Very little dynamite was used.

*New York.*—Emery deposits of the spinel variety occur east of Peekskill, Westchester County, and have been operated by various

companies since 1883.<sup>6</sup> The ore occurs on the border of an igneous complex composed of hornblende and olivine pyroxenite termed the "Courtland" series. The emery occurs in a region in which mica-schist inclusions are abundant, and is in sharply defined veins immediately associated with rocks containing sillimanite, cordierite, garnet and quartz. A characteristic of these schist inclusions is the great abundance of biotite found around the ore in many places. The two chief mines are the Dalton and McCoy. They are worked by open-cut methods, some pits being over 80 ft. deep. In recent years production has been maintained by two operators, the Smith & Ellis Co. and the Keystone Emery Mills, but the former was the only producer of American emery in 1935 and 1936.

### *World*

*Greece.*—The island of Naxos is principally made up of gneisses and mica schists alternating with crystalline limestones. The lenticular masses of emery, varying in width from 15 to 150 ft. and sometimes as much as 100 yd. long, are closely associated with the limestone. The best Naxos emery is dark gray, usually mottled with bluish specks or streaks of pure corundum, and is the hardest emery known. The best ore comes from Vothrie, 9 miles from the coast, on the northeast side of the island. Another important deposit is at Apiranthos, 7 miles inland, from which the ore is shipped at the ports of Sulinos and Mutzoma. On the northern part of the island it is mined near Yasso.

Emery of a similar mottled appearance and quality, but of lamellated structure, occurs on the island of Nicaria, and a dark blue emery is found on the island of Samos, near the Asia Minor coast, but these deposits are not so extensive as those of Naxos. The mineral is sometimes also found embedded in white marble.

*Turkey.*—Emery is obtained in Asia Minor from the province of Aidin, which embraces almost the entire basins of the Sarabat and Mender Rivers. Smyrna is the principal port and center of trade for the surrounding districts and islands. Railways extend from the city into the interior along the basins of the rivers named above.

The greater part of the region is underlain by pure white or finely granular crystalline limestones, which are interfoliated with chloritic and micaceous schists and gneisses. The emery deposits occur as pockets or lenticular masses in the limestones and vary from a few feet to 200 ft. in width, and up to 300 ft. in length. The mineral also occurs as a detritus resulting from the weathering of the rocks.

Extensive deposits have been worked on the Gumuch-Dagh mountain in the vicinity of Ephesus and from the slopes of Ak Sivri, which is about 100 miles southeast of Smyrna. The emery from the former locality is usually fine grained, dark blue to purplish in color, and the interior of the masses is free from micaceous inclusions, while that from the latter

deposits is coarse grained and much darker in color. Kayabachi is at present the center of a number of small producing mines, the ores from which are shipped from the port of Kulluk. Other centers are Thyra, Aphrodisia, Inai and Azizieh, the shipping point being Smyrna. The ore exported is branded according to these seaports.

Usually the emery ore possesses numerous fractures or cleavage planes, so that it is easily broken into blocks of suitable size for handling. The main source of supply has been the loose emery or boulders embedded in a compact red clay, which occurs in shallow depressions in the limestone.

At the beginning of the war, the Abbotts' Emery Mines Ltd., the largest operator, installed a wire-rope tramway system from its principal mines to a more accessible point near the coast, but the plant was seized and destroyed by the Turks. All of the nine or ten producing mines were closed during the war, but in recent years production has been substantial.

*Russia.*—Four deposits of emery, some of which are being worked, occur in the southern portion of the middle Urals northeast of the Kyshtym works, on the eastern shores of Irtyash Lake, at the southern end of which the Techensky crushing mill is situated. All the emery deposits are confined to bands of crystalline limestones in contact with granitic gneiss, and occur therein as lenses or bodies ranging from 15 to 100 ft. in length, with a maximum depth of 150 ft. below the surface.<sup>11</sup>

*Other Countries.*—A small output of emery has been maintained annually from Wildenreuth, Bavaria. Emery occurs in several localities in Australia, mainly near Crookwell, New South Wales; also in the West Kimberley district of Western Australia. A fine-grained emery occurs in the Department of Minas, Uruguay, and also near Deschnet, eastern Fars, Persia, but no production from these localities has been reported.

#### POLITICAL AND COMMERCIAL CONTROL

The small output of emery in the United States is due mainly to the somewhat inferior quality of the known deposits as compared with those in Greece and Turkey and also to the low cost of mining in the latter countries. The Government of Greece controls the sale of emery from that country, which is effected by tender, all supplies being collected in its warehouse on the island of Syra. One of the largest exporters of both Greek and Turkish emery is at Amsterdam, Holland, where the crude ores are crushed and graded. The crude ore is also sent to five crushing and grading plants in the United States and some in England. There are no crushing plants in Turkey and only one small one in Greece.

#### PRODUCTION AND CONSUMPTION

##### *United States*

Emery has been produced in the United States since the early eighties, the first output being from Chester, Hampden County, Mass. The



Whittles, Va., deposit was worked between 1917 and 1928. The Peekskill deposits, Westchester County, New York, have been operated since 1883 and at present (1936) production is being maintained by one company in this district. During the World War annual production in the United States was about 15,000 tons, but has since gradually dwindled and in recent years the output has been under 200 tons, the lowest on record, but increased slightly to 325 tons in 1936.

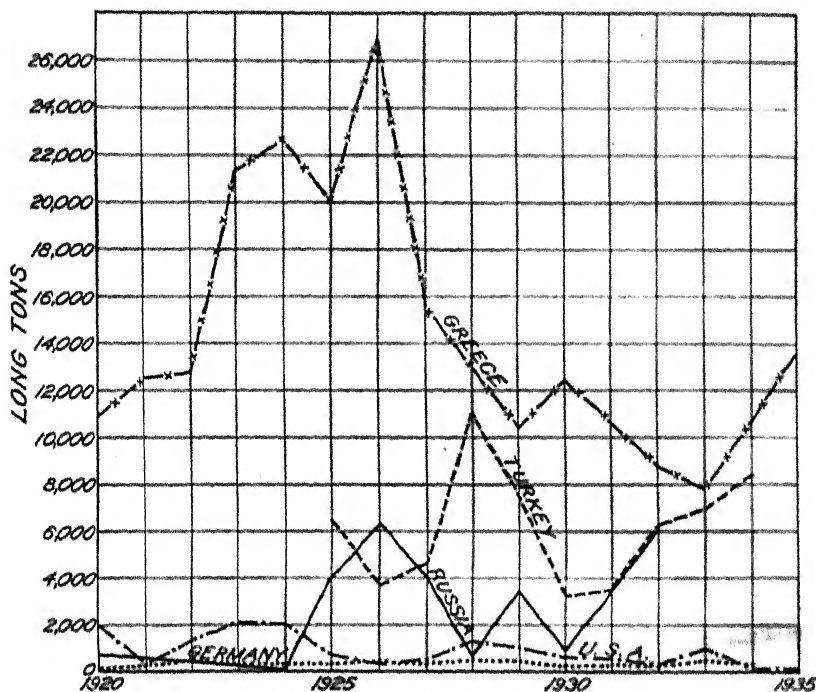


FIG. 1.—WORLD PRODUCTION OF EMERY, 1920-1935.

### World

Emery has been mined in Greece for several centuries, but was not extensively produced until 1870. The prewar production ranged from 8,000 to 13,000 tons annually, reaching its maximum of nearly 27,000 long tons in 1926, and after an appreciable decline it has now risen to about one-half the maximum. The Turkish production has in the past been considerably less than that of Greece, but has remained comparatively steady and is now not far behind. A chart of the world's emery production is given in Fig. 1.

### MINING METHODS

In the United States ordinary open-cast and underground methods of mining are employed in the Peekskill district. In Greece, mining operations are of the simplest character. The boulders or blocks containing



the ore, when not too large, are transported in their natural condition to the seacoast. The larger blocks are broken to a suitable size by means of hammers, sometimes with the assistance of heat and sudden cooling with water. Most of the present supply comes from the Liona and Mutzoma mines.

### PREPARATION FOR MARKET

All the Greek and Turkish emery is shipped in lumps ranging from the size of a marble to 25 lb. in weight.

In the United States there are five emery-crushing and grading mills in which the crude ore, both American and imported, is first crushed by jaw crushers and thence through a series of chilled rolls to  $\frac{7}{8}$ ,  $\frac{3}{8}$  and  $\frac{3}{16}$ -in., then to finer sizes in ball mills. The mica is removed by allowing the coarse grain to fall down a chute; an uprushing current of air blows the mica to one side into a separate compartment. The emery then passes over a series of long troughs, shaking screens, whereby the emery is carefully graded into about 30 different sizes. The oversizes are further reduced by means of small rolls, and return through the circuit.

In some plants the crude grain is washed with water in pans of the Chilean mill type, in which hardwood wheels revolve. This cleans off the adhering dirt, and the cleaned material is dried and graded. Although this washing process is more costly, a much purer and better cutting article is produced. The overflow from the washing pans, containing all the fines, flows through a series of long settling troughs. The settled material is then shoveled out into drying ovens, and this "flour" is further screened into three or four grades. The finest flour grades are made by drawing off the solutions at certain intervals of time, and drying the residue after final settlement. The 12 sizes from 6 to 46 mesh are termed "coarse grained" and the 12 sizes from 54 to 220, "fine grained" and there are four "flour" grades, from F to FFFF. There are also still finer flours, produced by decantation methods, which are used principally for optical work.

In the manufacture of emery paper or cloth, the largest size is No. 4 or 20 mesh and the following grading has been adopted:

Grade.....	4	3½	3	2½	2	1½	1	½	0	2/0	3/0	4/0
Mesh.....	20	24	36	46	60	70	80	90	120	150	180	220

The finer grades of paper keep their designation of multiples of F. In recent years acid treatment and roasting of the grain has considerably improved its abrasive qualities.

### MARKETING, USES, SPECIFICATIONS AND PRICES

*Marketing.*—The sale of Greek or Naxos emery is under government control and buying is usually effected through agents on a commission

basis, which includes the making of all shipping arrangements. The buyer pays the costs of weighing and lighterage, which average 4s 6d per ton. Exports of Naxos in 1936 were mainly to the Netherlands, although there was a fair tonnage to France, Italy and the United States.

The imports of Greek and Turkish emery into the United States from 1930 to 1936 are as follows: Greece 1500, 1137, 2, nil, 742, 1455 and 650 tons and from Turkey 2300, 966, 600, 262, 2319, 2835 and 4891 tons.

For many years there has been more demand for Turkish than for Naxos emery, except in 1931 when the introduction of the acid-treated and heat-treated Naxos grain stimulated sales of the latter.

*Uses.*—Naxos emery does not undergo detrimental physical and chemical changes under intense heat, and the grains are very hard and sharp, therefore this emery is the most suitable for the manufacture of grinding wheels. The Turkish emery is usually slightly softer than Naxos and the grains tend to break down under pressure. As it is fairly tough, it is best suited for the manufacture of emery cloth or paper, in the setting up of polishing wheels and in pastes and compounds. In finer sizes the loose grains, both Naxos and Turkish, are used in grinding and beveling of glass. There are, however, some deposits in Turkey that contain an emery said to be harder than Naxos and to be usable for manufacture of grinding wheels. The American emery, being appreciably softer than either is now used mainly in pastes and compositions.

*Specifications.*—The specifications for an emery depend upon the uses to which it is to be put. Pure corundum or manufactured abrasives are considered too hard or harsh for certain grinding and polishing operations and it is the softer constituents of emery that tone down the harshness of the admixed corundum and give the desired results. The emery should contain corundum, those having the higher proportion being best suited for grinding wheels and those with the lower proportion for polishing and for pastes. The emery for the former should be hard and tough, whereas for the latter a more friable emery gives a smoother finish.

*Prices.*—Quotations in the mineral markets for the past few years have been steady: American crude ore, first grade, \$10 f.o.b. New York or \$16 delivered to grinders; Turkish and Naxos, \$30 to \$40 per ton in 350-lb. kegs delivered to grinders. American grain 4½¢ and foreign grain 6 to 7¢ per pound f.o.b. grinders.

The recent United States import values were \$12 to \$13 per ton for Turkish and \$24 to \$25.40 for Naxos. The 1936 selling rates of Naxos were: first quality, large lumps, £4 8s; small lumps, £4 14s; second quality, large lumps £4 6s; small, £4; emery fragments (chips), £3 13s per metric ton. These prices apply to deliveries ex-warehouse at Syra.

## GARNET

The name "garnet" is given to a certain group of minerals possessing similar physical properties and crystal forms, though their chemical

compositions vary widely. The term is derived from the latin word *granatus*, meaning seedlike, because the crystals embedded in the matrix usually resemble seeds. Before the eighteenth century, the mineral was known as "granat."

### COMPOSITION

The garnet group comprises seven different species, all of which are silicates of aluminum, calcium, iron, magnesium, manganese or chromium, the different metals being replaceable one by the other. Because of the variety in their compositions, some garnets are unaltered by weathering while others become completely disintegrated. Very often other minerals, particularly quartz, mica and pyroxene, are included within the garnet crystals, and in some instances these are so finely disseminated that it is almost impossible to make a mechanical separation of the garnet. Varieties of garnet are as follows:

Almandite ( $3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) the commonest and andradite ( $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$ ), also quite common, range in color from deep red, brown to black. The colored varieties of andradite are melanite (black), demantoid (green), topazolite (yellow-green). Grossularite ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) may be white, pale green or yellow. Uvarovite ( $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) is emerald green. Pyrope ( $3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) ranges in color from deep red to black. Spessartite ( $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) is brown to red in color. Rhodolite, a mixture of two molecules of pyrope to one of almandite, varies from pink to dark red.

### PROPERTIES

*Color.*—As outlined above under different varieties.

*Hardness.*—Hardness varies from 6 (grossularite) to 7.5 (almandite, uvarovite and rhodolite), though some varieties of almandite are said to be 8.

*Crystal System.*—Cubic, commonly as rhombic dodecahedrons or tetragonal trisoctahedrons, or in combination of the two.

*Cleavage.*—Occasionally an indistinct dodecahedral cleavage is observed, but some species of almandite possess a pronounced laminated structure, which forms planes of weakness along which the mineral separates, but this parting has no relation to the crystal form and is not a true cleavage.<sup>20</sup>

*Fracture.*—Garnets possessing a glassy structure usually have a marked conchoidal fracture but sometimes the mineral tends to break into thin flakes (which are probably parting planes), while in other varieties the fracture is sharp and uneven.

*Index of Refraction* in grossularite is 1.735; almandite 1.778 to 1.830; andradite 1.865 to 1.94.

*Fusibility.*—High-iron garnets readily fuse to a dark glass—almandite at  $1315^{\circ}$  C.—while high-chromium garnets are unfusible before the blowpipe.

*Tenacity.*—Aggregates of crystals, or the laminated varieties, fracture readily into their component parts, but the solid and well formed crystals are very tough.

*Other Properties.*—Specific gravity, 3.5 to 4.2. Luster, vitreous resinous or dull. Transparent to opaque. Molecular weight: pyrope, 405; almandite, 499; andradite, 509. Streak, white. Dispersion, 0.24 to 0.28.

### ORIGIN AND MODE OF OCCURRENCE

Garnets occur as accessory minerals in a large variety of rocks all over the world, but are particularly common in gneisses and schists. In some instances they are present in such large quantities that the rocks are designated as garnet schists or gneisses. They also occur as contact-metamorphic deposits in crystalline limestones, pegmatites and serpentines, etc. The usual associated minerals are hornblende, mica and quartz, with feldspar and pyroxenes in smaller proportions. Little information is available as to the occurrence of garnet below 400 ft. in depth, because nearly all garnet mining has been confined to open-cut methods, although garnet is sometimes found in the gangue at moderate depths in mining other ores, such as iron and copper. Garnets occurring in contact-metamorphic zones, which are formed by the replacement of the sedimentary rocks, are of secondary origin, but it is probable that the garnet in pegmatites and granites is one of the original rock minerals and of primary origin.

Because they are more resistant to weathering and erosion than their associated rocks, the garnets often occur as a detritus of crystals in the immediate vicinity of the original rocks, or as rounded grains in river and sea sands. In sands, owing to their comparatively high specific gravity the garnets are usually concentrated by water action into beds or layers.

Garnets vary greatly both in size and in concentration. The crystals may be several feet in diameter—like those being mined in New York State—down to crystals smaller than a pin's head. They may occur very sparsely distributed or close enough to constitute 70 per cent of the rock. In some places there is high concentration of very small crystals as pockets or lenses and in others the garnet is in the massive form that does not disintegrate or break up into individual crystals.

### DISTRIBUTION OF DEPOSITS

Garnet in its various types is not an uncommon constituent of the rocks throughout the world, but deposits of high-quality abrasive are comparatively rare. The world's commercial abrasive garnet deposits

appear to be confined mainly to the American continent. Although there are numerous occurrences of possible abrasive garnet in other countries, little has been done towards their development, and there has been no recorded production outside America, except from Spain and small quantities from India and Madagascar. For commercial occurrences of gem garnet, see chapter XVI.

### *United States*

The supply of commercial abrasive garnet at present (1936) comes from two deposits in New York State operated by the Barton Mines Corporation and by the Warren County Garnet Mills, Inc., and from one deposit in New Hampshire operated by the Davenport Garnet Co. Between 1922 and 1925, when production was at its peak, there were several other operators in these states as well as one in North Carolina.

*New York, New Hampshire and North Carolina.*—New York State is the principal producer, the high-quality material of the Adirondack district being considered the world standard for abrasive garnet. Garnetiferous rocks occur over a wide area in Warren, Essex and Hamilton Counties. At the Barton mine the mineral is in fairly well developed crystals from 1 in. to 3 ft. in diameter, and occasionally in large masses almost devoid of individual crystallization. The rocks are mainly metamorphosed gneisses and the garnet content seldom above 15 per cent, except in deposits in which massive aggregates are present. In New Hampshire, the garnet as crystals the size of a pea or slightly larger constitutes an average of 50 per cent of the porphyritic biotite schists in which they occur.

The following brief descriptions of the New York, New Hampshire and North Carolina deposits that were being operated in 1925 are herewith quoted from Myers and Anderson's report.<sup>20</sup> These descriptions give the locations, geology, characteristics of the garnet and some methods of mining and handling the ore.

*The Barton Mines Corporation.*—The quarry of the Barton Mines Corporation is on Gore Mountain, about 11 miles by road from the village of North Creek. The most characteristic feature of the dark gray, massive rock quarried is the garnet crystals themselves, which give the rock a porphyritic texture. Mineralization is simple, as hornblende constitutes nearly 40 per cent of the rock mass, the remainder being divided between orthoclase and plagioclase feldspars, pyroxene and mica. Small amounts of pyrite and magnetite are also present. The garnet content of the ore averages about 13 per cent and occurs in crystals of unusual size. Single crystals a foot in diameter are common and individual ones from 30 to 36 in. in diameter have been found. The crystals have a very pronounced laminated structure by which they are divided into plates from a sixteenth to a quarter of an inch in thickness.

The garnetiferous rock has undergone considerable alteration at the surface, and the first mining was in this oxidized zone from which the garnet could be readily recovered. Later quarrying was started in the unoxidized rock, and with the erection of a modern concentrating mill in 1924, the quarrying was placed on a systematic basis. The quarry

now consists of a series of open pits which are being developed into regular benches. Ten-foot holes are drilled with jackhammers and these are shot with 40 and 60 per cent gelatin. Boulders are blockholed with small charges of dynamite. The broken ore is loaded in three-ton cars with steam shovels and hauled to the mill with a gasoline locomotive. In breaking the ore in the quarry many of the garnet crystals are shattered. The largest fragments of clean garnet are picked and sacked for immediate shipment.

A new lower level in the mine has now developed ore at a depth of 380 ft. below the surface. For further details see the article by T. S. Mennie.<sup>18</sup>

*The North River Garnet Co.*—The quarry and mills of the North River Garnet Co. are located on the eastern side of Thirteenth lake in Warren County about 10 miles from North Creek, the nearest shipping point. The gneiss quarried carries 4 to 8 per cent garnet in crystals having a maximum diameter of three inches. Hornblende and feldspar constitute the most important gangue minerals. The quarry is in a large projecting knob of gneiss, and has a maximum diameter approaching 300 ft. The jointed structure of the rock is highly developed, and the horizontal partings are utilized as the base of small benches in quarrying. The rock is drilled to a depth of 15 ft. and holes are sprung and then loaded with 60 per cent ammonia dynamite which is fired with a blasting machine. Large blocks are reduced by blockholing and the broken ore is loaded either by hand or by steam shovels to quarry cars which run to the head of the mill, a maximum distance of 200 yards.

For further details see article by F. E. Wormser.<sup>23</sup> The North River Garnet Co. was amalgamated in 1927 with the Barton Mines Corporation, when mining and milling operations were restricted to the latter property. For a number of years the Barton Mines Corporation has continued to be the principal producer of garnet.

*Warren County Garnet Mills.*—The Warren County Garnet Mills, Inc., operate a number of small scattered quarries in the vicinity of Weverton and Johnsburg, 6 miles southeast of Gore mountain. The garnet occurs in broad bands in a biotite gneiss, much of it being in massive aggregates which in places constitute nearly the whole rock. The garnet ore is removed from shallow excavations, seldom exceeding 8 feet in depth. The rock is drilled by hand, with a single-jack, blasted, sledged and hand-picked, and trucked to the mill. The garnet content of the ore going to the mill is high, varying from 30 to 60 per cent.

This property has been operating for a number of years, maintaining a small but steady output.

*The Wausau Abrasive Co. (Davenport Garnet Co.)*—The mine and mill of the Wausau Abrasive Co. is located in North Wilmot, Merrimack County. The garnet is present as numerous small crystals,  $\frac{1}{4}$  to  $\frac{3}{8}$  in. in diameter, forming 40 to 60 per cent of the total rock mass. Feldspar and biotite mica are the most prominent gangue minerals. The quarry is approximately 180 by 100 ft. with a maximum depth of 25 ft. Holes are drilled to a depth of 6 ft. and shot with 60 and 75 per cent gelatin. Boulders are bulldozed, and the broken rock is loaded by hand into cars, which are hoisted up an incline. The cars are then trammed by hand to an ore bin on the hillside above the mill. The ore from the bin is fed to a jaw crusher which crushes to  $1\frac{1}{4}$  in. The crushed ore falls into a loading bin which loads the buckets of an aerial tramway. This tramway conveys the ore to the mill, a distance of 1200 feet.

After the reorganization in 1929, the company acquired the name of

Garnet Products Co., a mining subsidiary of the Wausau Abrasive (sandpaper) Co., but since 1935 has been known as the Davenport Garnet Co. For full details of the New Hampshire garnet deposits, see the recent article by L. C. Conant.<sup>14</sup>

The deposit of rhodolite garnet at Sugar Loaf Mountain,  $2\frac{1}{2}$  miles south of Willets, N. C., has been worked at intervals by the Rhodolite Company, and a considerable tonnage of garnet was recovered between 1900 and 1926. The mineral, in small crystals of less than  $\frac{1}{2}$ -in. diameter, occurs in a large body of quartz feldspar mica schist. The average content is 20 to 25 per cent garnet with local concentrations as high as 60 per cent. A mill was erected in 1925 but for the past 10 years there has been no production.

*Other States.*—The following is a brief account of the garnet activities in other states during the past five years, but no sales have been recorded. Prospecting work was done in 1930–1931 by the Pacific Coast Garnet Co. on an amber colored andradite garnet deposit northwest of Cadiz station, San Bernardino County, California. For the past three years J. I. Fassett has been prospecting a garnet property at the Sunny Day mine, near Indio, Riverside County, California, but although a few tons of rock have been mined, there have been no shipments. The Vermont Mica Co. during 1931–1932 operated a micaceous gneiss carrying about 14 per cent garnet at Gassets, Vt. The company marketed the mica and stored the garnet for future sales. In 1936, the Celo Mines Inc., Burnsville, N. C., produced a small amount of garnet as a by-product in the concentration of kyanite rock. The pre-Cambrian schists of North Georgia constitute a possible source of abrasive garnet and are said to be worthy of investigation.

In Alaska, at Rothsay point, which is at the entrance to the Stikine River opposite Wrangell, beautifully formed, almost transparent claret colored crystals,  $\frac{1}{2}$  to 1 in. in diameter, occur in a fine-grained dark gray mica schist. The garnets are studded throughout the schist at fairly close and regular intervals and readily fall out when the rock is fractured. The garnets possess excellent abrasive qualities and about 10 to 15 years ago small shipments were made to various places on the west coast.

### *World*

Garnet occurs in many countries throughout the world, but during the past decade production of garnet outside the United States has been comparatively insignificant. In recent years a small output has been maintained from Spain and India (garnet sands).

*Canada.*—Garnetiferous rocks, mainly gneisses, occur in many parts of Canada. In some localities, particularly in southern Quebec, garnets are a common rock constituent covering many square miles of territory. Prospecting has been carried out intermittently on several deposits, but the only output of consequence has been from a deposit in Ashby Town-



ship, Lennox and Addington Counties, Ontario, when in 1923-1924 about 1200 tons of rough concentrate was shipped. A deep red garnet of exceptionally high quality occurs intimately associated with pyrrhotite near Labelle, 100 miles north of Montreal, Quebec. Prospecting has been carried out intermittently during the past 10 years but only small trial shipments have been made. The ore occurs in a garnetiferous gneiss. The garnets of the latter are an inferior abrasive and are difficult to separate from the high-quality mineral except by hand-picking. A few car lots of garnet rock obtained from a neighboring deposit near Labelle were crushed in a mill erected on the property during 1934 and shipped for sandblasting purposes. Prospecting work has also been conducted on a garnet deposit at Depot Harbour on Parry Island, Ontario; near Sudbury, Ont. and at Cheggogin Point, Yarmouth, Nova Scotia. Full details of all the known Canadian garnet occurrences (about 100) will be found in the Mines Branch Bulletin.<sup>13</sup>

*Spain.*—The Spanish garnets, which are a pale pink, occur as small rounded crystals in the alluvial deposits of the Province of Almeria. The garnets are inferior to the American and when crushed do not yield the full range of the sizes required by users. At one time imports of these garnets to the United States amounted to 500 to 3000 tons annually, but have steadily dwindled in the past decade, and ceased altogether since 1933.

*India.*—Garnetiferous gneisses and schists occur in many parts of India. Many years ago an attempt was made to market a massive garnet rock in the Hazarbagh district of Behar, but it did not prove remunerative. No regular garnet industry has been established and the supply now comes from local concentrations of river and sea sands. The principal places at which production has taken place are in the Tinnevely district of Madras, where over 1000 tons of garnet sand was produced in 1914; Nellore in the Deccan, and a number of different localities in Mysore. For the past few years there has been a fairly steady annual production of between 200 and 300 tons of garnet sand from the Tinnevely district.<sup>14</sup> There are numerous deposits of gem and ornamental garnets in India and production has been fairly steady.

*Other Countries.*—Small and irregular shipments have been made from Madagascar. Tests have been conducted on garnet from deposits in Ceylon, South Africa, Malawe Hill in Nyassaland, British Somaliland, from an island in St. Huberts Bay off the Labrador coast, etc. Near Prague, Czechoslovakia, alluvial garnet (pyrope) has been washed and concentrated in crude jigs. Mittleburge, Czechoslovakia, was at one time the world center for gem garnet, 10,000 men being employed.

#### POLITICAL AND COMMERCIAL CONTROL

The abrasive garnet industry, which reached its peak in 1923-1924, has dwindled regularly and appreciably, owing largely to the competition



from manufactured abrasives. The comparatively small output between 1931 and 1935, however, increased about 75 per cent during that period; while the output of the competitive manufactured products, silicon carbide and fused-alumina abrasives, increased 144 per cent for the same period. The United States is now the only producer of mined garnet that is crushed and graded, and the product is recognized as the world standard. Imports of garnet into the United States, which at one time were quite substantial,

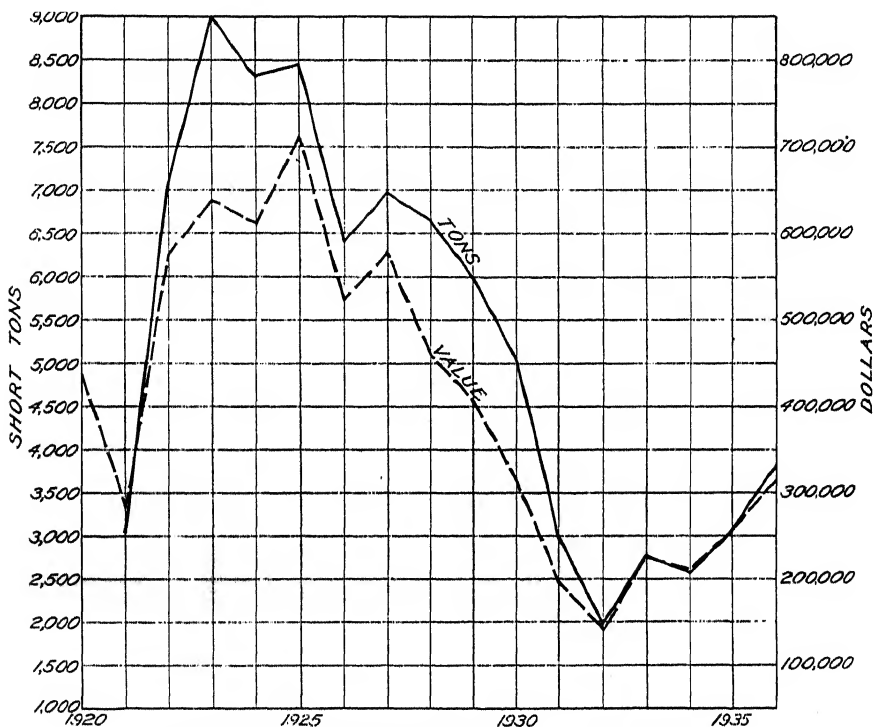


FIG. 2.—UNITED STATES PRODUCTION OF GARNET, 1920-1936.

have now ceased entirely. The available supply and the capacity of existing mills are far greater than the present demand. The principal sandpaper manufacturers in the United States own or control the operating mines.

Crude garnet ore and ungraded concentrate enter the United States on the free list under Paragraph 1619 of the Tariff Act. Graded and specially prepared garnet is dutiable at 1¢ per pound under Paragraph 1415.

#### PRODUCTION AND CONSUMPTION

*United States.*—Garnet was first employed as an abrasive in the United States and became commercially important about 1880, when it was used

as coated abrasive by Herman Behr and Co., of Brooklyn, N. Y., and its superiority over flint and the California red carnelian for sanding hardwood was quickly established. The first mining operations were conducted by H. H. Barton, of Philadelphia (to whom the initial developments of the abrasive garnet industry are largely due), in the Adirondack section of New York State, followed immediately afterwards by the development of a deposit by Herman Behr at Boothwyn, Delaware County, Pennsylvania, and later, of deposits in Connecticut. The first large-scale milling of garnet ores was done by F. C. Hooper, of the North River Garnet Co., North River, N. Y., in 1893. After the exhaustion of the deposits in Pennsylvania and Connecticut, production was confined to New York, New Hampshire and North Carolina. The New York mines are now the world's leading producers.

United States production of abrasive garnet did not attain commercial importance until after the milling operations in 1893 referred to above. The total garnet production from 1893 to 1936 amounted to 192,889 short tons.

Fig. 2 gives the output of the United States from 1920 to date, and illustrates the decline since the peak year of 1923.

*Other Countries.*—The production of abrasive garnet in countries outside the United States has been small and intermittent. The following is the record in long tons since 1920:

Year	Long Tons				
	Canada	India (Garnet Sand)	Spain	Japan (Garnet Sand)	Madagascar
1920		20	195		
1921		5	5		
1922				3,351	10
1923	1,116	3	966	3,529	5
1924	.321		1,094	3,474	
1925				3,484	
1926		14			
1928		480			
1930		7			
1932		147			
1933		295			
1934		225			
1935			179		

### PROSPECTING, EXPLORATION, AND MINING METHODS

Because present demand for abrasive garnet is comparatively small and is greatly exceeded by the known potential supply, special search for new deposits would not appear to be necessary. No deposits need be

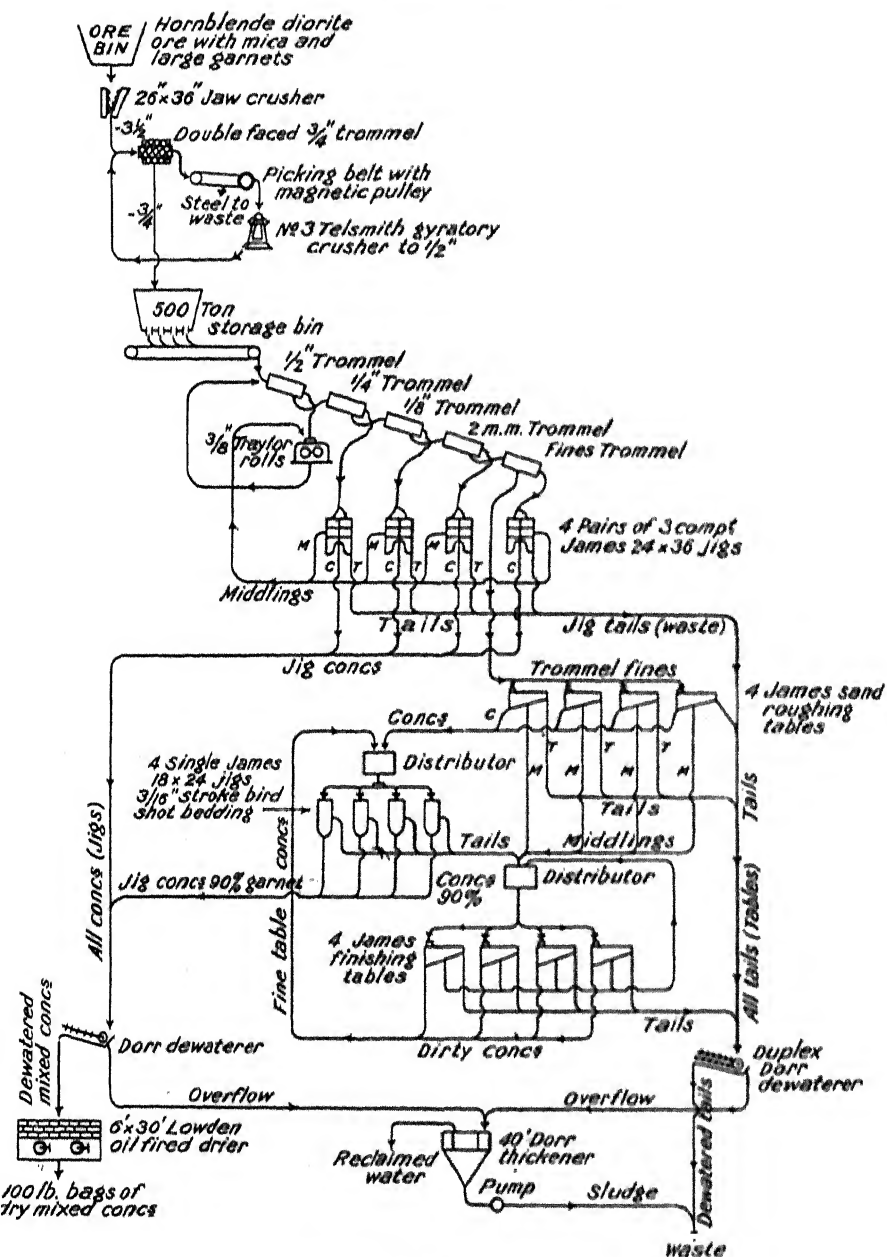
considered unless preliminary examination indicates that the garnet will adequately fulfill the qualifications as outlined later in this chapter. If the surface indications are satisfactory, samples for tests should be taken, if possible, at a depth below the influence of weathering.

Garnet is usually mined by open-quarry methods, though in some instances it has been extracted by underground stoping. The usual procedure is followed, though in deposits containing very large crystals excessive shattering through the use of too much powder should be avoided and hand-picking is advantageous. If the garnet occurs as concentrated bands or zones, the deposit should be cross-trenched and the best zones followed. The mining practices of some of the producers in the United States is briefly outlined under the descriptions of the individual properties.

### PREPARATION FOR MARKET

Before being used for the abrasive coating of papers and cloths, the garnet must be concentrated and graded. Being a heavy mineral (av. sp. gr. 4.0), garnet is usually concentrated by ordinary gravity methods, either wet or dry. The former is the general practice and the more suitable for the majority of the ores. The main object in concentrating garnet for the paper trade is to obtain a material with as large a mesh and as pure as possible, and to avoid fines. The manufacturers of coated abrasives in the United States usually prefer to do their own grading (sizing), so they require coarse material from which varying proportions of any size can be obtained by crushing, but in crushing, fines are unavoidably produced. When standard grading is more general, these grades may possibly be made direct in the course of concentration, but the present practice in milling is to mix together and bag all the grades obtained. The degree and stages of crushing are of the utmost importance, therefore, and care must be taken that the coarse particles of garnet are free from attached impurities. Therefore it is necessary that preliminary concentration tests be conducted on a garnet ore in order to determine the most efficient degree and type of crushing before the erection of the mill. A flowsheet diagram of the leading garnet producer of the United States in 1925 is given in Fig. 3. Some changes and improvements have been made since then, but these illustrate the careful crushing and screening, followed (in the wet process) by jigs and table concentration, that are necessary to preserve the large garnet grain and reduce fines to the minimum. Magnetic separators are used in the dry stages to extract the magnetite, pyrrhotite and included iron. The dry process differs essentially from the wet in the use of an air concentration table of the Sutton, Steele & Steele type. A preliminary extraction of the mica is accomplished by allowing a stream of the dry crushed ore to encounter a crosscurrent of air that deflects the lighter particles of mica and excess fines.

# INDUSTRIAL MINERALS AND ROCKS



*Ore, Large laminated and masses of garnet crystals which average 12% of the rock composed principally of hornblende with some feldspar, pyroxene and mica*

FIG. 3.—FLOWSHEET OF 250-TON GARNET MILL, THE BARTON MINES CORPORATION, NORTH CREEK, WARREN COUNTY, N. Y., IN 1925.

*Impurities.*—Quartz, feldspar and mica, being considerably lighter than garnet, should be entirely removed during the process of gravity treatment. Iron pyrites and pyrrhotite can be removed by careful tabling and the latter by ordinary magnetic separation. Hornblende is one of the commonest impurities and, as its specific gravity (3.4) is close to that of garnet, it is rarely, if ever, entirely eliminated from the final concentrates. It can, however, be effectively removed by means of the Ulrich magnetic separator.<sup>13</sup> Hornblende, though softer than garnet, is nevertheless fairly hard and in small quantities is not detrimental. The black grains almost invariably present in the commercial red or pink garnet-coated papers and cloths are hornblende.

Details of garnet flowsheets, machinery and concentration tests will be found in various reports.<sup>13, 17, 18, 20</sup>

*Heat-treatment.*—The toughness, fracture and color of iron garnets are improved by heating the grain at about 800° C. for about 12 hr. and then quenching. This treatment, covered by U. S. Pat. 1836448, Sept. 22, 1930, and by U. S. Pat. 2029253, Aug. 30, 1935, is successfully employed by several manufacturers of abrasive-coated papers and cloths.

*Grading.*—Grading consists of alternately crushing and screening the concentrate in order to obtain the full range of grades (mesh sizes) required by the sandpaper manufacturers.

## TESTS AND SPECIFICATIONS

*Qualifications of Abrasive Garnet.*—Garnets vary considerably as to color, hardness, toughness and method of fracture. For the best abrasive, it should be as hard as possible, at least 7.5 (quartz is 7.0). When the garnet is crushed the grains should break into sharp, angular fragments without curved or rounded edges. The mineral should not break too easily, but it should be brittle enough so that the individual grains will eventually break and form new cutting edges rather than become rounded under the strain of work. Thin or slivery grains do not arrange themselves correctly because they tend to lie too flat when applied to the glued surface of paper, thus presenting a smooth, noncutting surface, or they protrude above the surrounding grains and tend to scratch. The crushed garnet grains should have a high capillary attraction, so that the glue will completely cover and adhere to them when they are being fastened to the paper or cloth. The color does not seem to have any particular bearing on the abrasive qualities, but the deep red or wine colored mineral is always preferred. In order to obtain the full range of grades necessary for coated papers, the garnet should be capable of being broken into comparatively large (size of a pea), clean and solid pieces free from embedded impurities, and with the minimum amount of fines. Therefore deposits that contain garnets of small crystals are of little or no commercial value for sandpapers, no matter how great the garnet content of

the rock may be. Granular garnet usually breaks into rounded grains; other deposits containing large crystals that are badly shattered, or crystals containing embedded impurities, would with little pressure crumble almost to dust. The compact, massive garnet might be used commercially, but comparatively little experimental work has been done on that type. Massive garnet, however, is almost invariably off-color, and the toughness and hardness of the crushed grains are usually inferior to those of solid garnet crystals. The grains in garnet sands are too small and they are rounded by erosion and water action.

Briefly, therefore, the best abrasive garnet comes from deposits of clean, unfractured, individual deep red crystals at least the size of a pea, but preferably larger. The recovery from the average types of deposits should be at least 10 per cent of such garnet in order to be commercially valuable. Up to the present, the highest quality of abrasive material has been obtained from the large, laminated crystals or boulders of red garnet like those in New York State. The kinds used for abrasive purposes are all iron garnets. Almandite is the commonest, but andradite and rhodolite are also used.

*Tests for Abrasive Utility of Garnet.*—There is no efficient method of testing the abrasive quality of garnet or of any other loose-grain abrasive. The real test is in its practical application. There are, however, several rough tests and examinations that serve to indicate their abrasive possibilities. The size, fracture, shape and purity of the grains, as outlined above, can be determined or compared by the microscope. The *toughness* of different garnets may be roughly compared by reducing them to the same grade (No. 1) and drawing a knife blade over a small quantity placed on a piece of steel or glass. Soft garnets will drag and soon break up into powder, but the knife will ride over the tough particles without appreciably reducing their size.

*Capillarity.*—This test depends on the capillarity of crushed garnet and serves to indicate its tenacity when applied to the glued surfaces of the paper or cloth. The higher the capillarity, the tighter will each particle adhere when coated with glue. In making comparisons care should be taken that the grains are of the same mesh and are absolutely dry, clean, and free from dust. The apparatus consists simply of a glass tube about 10 in. long, 4 or 5 mm. inside diameter, blocked at one end by a piece of fine screen.<sup>x</sup> The tube, which should be dry and clean, is partly filled with the sample to be tested, gently shaken down, and the closed end is dipped into a known height of water (about  $\frac{1}{2}$  in.). The water will rise up through the screen and into the garnet, and after 3 to 4 minutes the tube may be removed from the water and the dry garnet poured out. The remainder, which adheres to the inside of the tube, is measured. The height of water into which it was placed should be deducted.

A capillarity scale of the different sizes is given in the Mines Branch, Canada, report.<sup>13</sup> Briefly, the rise in centimeters for the coarse sizes is about 4.0 cm.; for the medium, about 8.0 cm., and for the fines 13.0 cm.

*Testing Machines.*—After a garnet has passed the above preliminary test, it may be tried out by applying the graded grain to a belt or disk. The glue used and the method of adhering the garnet to the backing is almost as important as the quality of the abrasive itself, so that comparisons should preferably be made only after the test samples have been made by a manufacturer of coated papers. The machine used by the Mines Branch, Ottawa, consists of a wooden drum 1 ft. in diameter and 1 ft. wide, around which the coated paper is stretched. A weighed block of hardwood to which are attached a lever and weight (to give the required constant pressure) is placed on the drum, which is made to revolve at a certain speed and time, the wooden test block moving gradually across the face of the drum during the operation. After each test the paper is examined for condition and the wooden block weighed to ascertain the loss. A strip of standard paper of the same grade (mesh) as the test strips is used for comparison. The methods and results of the testing of garnet for both sandpaper and sandblasting are given in various reports issued by the Ore Dressing Division, Department of Mines, Canada.

#### MARKETING, USES AND PRICES

Probably about 90 per cent of the abrasive garnet is used for the manufacture of abrasive-coated papers and cloths and the remainder as a lower priced material in the form of loose grain for various purposes, such as surfacing and polishing marble, slate, soapstone, and other soft stones; in some sandblast operations and a very small amount for the surfacing of plate glass.

*Papers and Cloths.*—On the American continent garnet-coated papers and cloths are used in the woodworking industries, particularly for hardwoods. In abrading softwoods, garnet and quartz papers appear to be nearly equally efficient, as both are soon clogged with the wood particles; consequently there is no advantage in the higher priced garnet. The recent introduction of open-coated papers, however, largely overcomes this trouble. In hardwoods the superiority of garnet over quartz is most pronounced and the cutting efficiency of the former is said to be from two to six times that of the latter. These papers are also used for the finishing of hard rubber and celluloid, for felt and silk hats, and as fine disks in dental work. They are employed extensively on leather, particularly in the boot and shoe industry for the scouring of heels and soles. In recent years fine grits of waterproof garnet papers have taken the place of pumice in the rubbing down of varnished and painted surfaces, especially automobile bodies. Garnet cloths are sometimes used for the softer metals.

The garnet-coated abrasive is used in the form of belts, covers for drums, disks, and as small sheets in hand work. The different grades of garnet used on these papers and cloths range from No. 5, the coarsest, which is about 15 mesh, to 7/0, which is about 220 mesh.

There are about ten manufacturers of abrasive-coated papers in the United States, two in Canada, and several in England, France, Germany, and other European countries. Details of the manufacture of coated papers are given in part IV of the Mines Branch Abrasives report.<sup>25</sup> The recently introduced method of electrostatic coating is meeting with success. In this process an electrostatic machine causes the grain to jump up and embed itself in the wet, glued surface of the moving backing. It is claimed that the grains stand up on their edges and are more evenly surfaced, owing to individual grain repulsion. This is a distinct advantage over the old method of coating, particularly if flat or slivery grains are present.

*Loose Grain.*—A small amount of garnet grain is bonded into wheels made by low-temperature processes which are employed for grinding glass and some metals. Some sales are made annually within the United States and Canada for crushed and sized garnet ore for sandblasting stone monuments (inscriptions) and on certain metals. A good, tough garnet from very rich deposits that would not require the expense of concentration might prove an efficient competitor of silica sand or of the more expensive metallic or manufactured abrasives.

*Glass Surfacing.*—The excess fines produced in manufacturing abrasive coatings, as well as finely crushed and water-settled garnet ore, was utilized for some years in the United States for surfacing plate glass in the stage between the coarse sanding and the final rouge polishing. Garnet was introduced for this purpose in 1914 and between 1925 and 1934 a fair tonnage was consumed by the glass industry. The Ford Motor Co. was the largest user, and operated its own deposit at Danbury, N. H., solely for this purpose, but in 1935 the company discontinued this use of garnet and reverted to graded sand. It is believed that very little garnet is now being used for glass surfacing.

*Gem Garnet.*—Clear, flawless garnets of various colors are extensively used for ornamental purposes. Between 1883 and 1920, the value of gem garnet produced in the United States varied from \$2,000 to \$22,000 in a year, the high values being obtained from the rhodolite garnet in North Carolina during 1900 and 1901. The output in the United States has dwindled to a figure so unimportant that no records have been kept since 1921. A large quantity of garnet is used for the jewels of the cheaper watch movements, but none has been produced in America for this purpose except a small amount during the World War, because the foreign supply has been abundant and its prices lower than the cost of domestic



production. Further details are given in chapter XVI and also in U. S. Bureau of Mines *Bulletin* 256.<sup>20</sup>

*Markets.*—The demand for garnet (which is indicated under Uses) has dropped steadily and appreciably since the peak year of 1923, owing to competition from manufactured abrasives. A small increase since 1931 has been due mainly to general improvement in business and perhaps to a small extent to the improvement in garnet grain through the heat-treating process and electrostatic method of application.

In Europe garnet is not so extensively used as on the American continent. This may be attributed to the inferior quality of the Spanish garnet, to the high price of the American, and to the use of chalk flint, which is cheaper than garnet and occurs in great abundance in England and in France. It is superior to the American so-called "flint" (which is really quartz) and is almost equal to garnet in its abrasive qualities. The European manufacturers of coated abrasive require graded grain, whereas the American manufacturers buy concentrates from the garnet producers and grade it themselves. The Barton company recently installed a grading plant at its North River mill.

*Prices.*—The price of the best American garnet in the form of a high-grade mixed concentrate (over 90 per cent garnet), free of fines, has remained constant for the past decade at about \$85 and lower grades \$60 per ton in bags of 100 to 150 lb. f.o.b. shipping point; glass-surfacing fines, \$40 to \$45. The finished and graded grains vary from 4¢ to 8¢ per pound, depending on grade or size of grain. The inferior kinds of garnet, such as the Spanish and low-grade concentrate, sell for about \$50 per ton.

#### SILICEOUS OR OTHER NATURAL ABRASIVES

Silica in many forms is used for abrasive purposes; i.e., flint, quartz and quartzite, chert, sandstone, sand, silt, amorphous silica, tripoli, diatomite, rottenstone and siliceous clays. These materials depend mainly upon the free silica and sharpness of the grains for their abrasive properties.

The abrasive uses and the common forms of silica as well as some other natural rock and materials are briefly listed in the table shown on p. 34.

Grindstones and pulpstones are often classified together under one heading, particularly for import and export figures. Although both are made from sandstone they are used for entirely different purposes and deposits that furnish the one rarely, if ever, furnish the other. Therefore these materials, as well as sharpening stones, millstones, etc., are reviewed separately.

#### GRINDSTONES

Natural grindstones are made from certain sandstones that occur throughout the world. The proper selection of the sandstone is of the

greatest importance and depends on the use to which the finished grindstone is to be applied. The suitability of a sandstone for the grinding of different substances depends on: (1) the percentage, as well as upon the character of the cementing materials such as silica, lime, clay, iron oxides, etc., (2) the size and shape of the abrasive (quartz) grains.

ABRASIVE USES	TYPES OF SILICA USED
Grindstones, pulpstones and sharpening stones	Massive sandstone from very fine to moderately coarse-grained. Also novaculite, fine-grained schist and siliceous shales
Millstones, burrstones, chaser stones	Cellular quartzite, fine-grained quartzite, quartz conglomerate, granite, silicified limestone
Tube-mill grinding pebbles	Rounded flint, quartzite and granite pebbles, also artificially rounded quartzite blocks
Tube-mill lining	Chert, flint and quartzite in dense, solid blocks.
In sandblast work	Quartz, quartzite, sandstone, and sand crushed or disintegrated into sharp or round grains of uniform size.
For sawing and polishing marble, granite, etc.	Sharp and clean quartz graded into various sizes.
In sandpaper	Quartz, quartzite, flint, sandstone, and sand; coarsely ground and sized
Lithographers' graining sand	Medium to fine sand or coarsely ground silica, and tripoli.
Wood polishing and finishing	All forms of silica ground to medium fineness.
In scouring and polishing soaps and powders	Pumice, volcanic dust, quartz, quartzite, flint, chert, sandstone sand, tripoli, rottenstone, diatomite, feldspar, all in finely ground state.
Metal buffing, burnishing and polishing	Ground tripoli, and other forms of ground silica.
In tooth powders and pastes.	Various forms of pure silica, finely ground.

### DISTRIBUTION OF DEPOSITS

Although there are many deposits of sandstone, only a few are suitable for the production of grindstones. Carboniferous sandstones appear to be the most productive of the formations, as the producing quarries of the United States, eastern Canada, England, Germany, etc. are mainly of Carboniferous age. The thickness of the bedding as well as the closeness and uniformity of the cross jointing further determines the suitability of the sandstone. No matter how good the physical properties of the stone may be, the deposit is useless unless the beds are thick enough, and the joints far enough apart, to ensure that large grindstones or pulpstones can be cut and dressed from the quarried blocks.

*United States*

The bulk of the grindstones comes from the state of Ohio and a small amount from West Virginia; in the past it came from Michigan.

*Ohio.*—Sandstones from which the grindstones are obtained occur throughout the major portion of the state. The northern and western limits stretch easterly from the northeast corner of the state along and close to Lake Erie shores as far as Norwalk, 70 miles west of Cleveland, and thence south till they reach the Ohio River on the south.

The sandstones in Washington County are known as the Dunkard series and rank among the most important sources of grindstones. They are blue-gray to yellow, are of loose, medium-fine grits, being slightly finer than the celebrated stones from Newcastle, England, which otherwise they resemble. They are principally used for grinding-machine knives, saws, and thin steel tools. In the southern area the bulk of the present output of grindstones is maintained by four or five producing companies in the vicinity of Marietta and Constitution on the north bank of the Ohio River.

Berea, west of Cleveland, in the northern part of the state, is another center of the grindstone industry, there being numerous quarries within a radius of 15 miles. The stone is yellow-gray, of a coarse grit, and usually contains over 90 per cent silica. At present the principal quarries are at Amherst and Kipton, Lorain County and at Euclid, Cuyahoga County. Only a few grindstones are quarried at Berea, but raw material from many localities is sent there to be made up into grindstones.

The Amherst stone is buff, friable and soft. It is specked with iron, oxidized to limonite, which is loosely contained between the grains of quartz. The solid individual grindstone beds are about 8 ft. thick, with a total thickness of about 40 ft. The best stone occurs in huge lenses or "boulders," and sometimes several hundred feet long and 100 ft. thick. A fair production of grindstone is being maintained by one operator at Layland, Coshocton County. Other sandstones that have been quarried in the past are: the Euclid stone, a very hard, fine-grained, blue grit, which occurs in beds of about 20 in. and is used mainly as whetstones, or as a polisher for removing scratches made by the ordinary grindstones, and for grinding shoulders of knives; the Independence grit, which is coarse and sharp, used for spring and file grinding; the Massillon grit, from Stark County, similar to the Independence; the Tippecanoe grit, from Harrison County, which is fairly loose and hard and is used for grinding springs, files, and heavy forgings.

*West Virginia.*—Grindstones are now produced only to a small extent from the southerly extension of the Ohio sandstones of the Dunkard series in the vicinity of Ravenwood, Jackson County, and St. Mary's, Pleasant County. They are being worked by the Constitution Stone

Co., one of the principal producers of grindstones. (The company's main output is from Constitution, Ohio.) There are, however, many abandoned quarries on the south bank of the Ohio River. The sandstone occurs in blue and brown layers and in many places contains considerable mica.

*Michigan.*—Until comparatively recently, grindstones were produced at Grindstone City and Port Austin, in the Huron district, from fine-grained, uniform, blue-gray beds of sandstone containing numerous flakes of silvery mica. At one time the Huron grit was extensively used for grinding mowing-machine knives, cutlery and tools requiring a fine edge.

### *World*

*Canada.*—The quarrying and manufacture of grindstones is one of the oldest industries in Canada. In the Maritime Provinces there are upwards of a hundred old sandstone quarries which have at some time been worked for grindstones. The industry was at its height at the end of the last century, and has since steadily declined, owing originally to the opening of the Ohio and other quarries in the United States and latterly intensified by the introduction of manufactured grinding wheels. The main centers were on the New Brunswick and Nova Scotia shores of the Cumberland Basin off the Bay of Fundy and also along the south shore of the Bay of Chaleur and at Newcastle, N. B. The Read Stone Co., Sackville, N. B., has been in the grindstone business for almost a hundred years. At present it is the only producer, maintaining a small output from Stonehaven on the Bay of Chaleur, N. B., and from Quarry Island, Pictou County, N. S. Details of Canadian grindstone industry will be found in the Mines Branch report.<sup>28</sup>

*England.*—In the trade the stones of England appear to be roughly divided into three classes, referred to as: (1) Newcastle stones, (2) Derbyshire or Peak stones, and (3) Yorkshire stones. These designations, however, do not necessarily indicate the locality of origin of the stones.

The Newcastle grindstones are obtained from thick-bedded, light gray and yellowish sandstones of the Coal Measures at various localities near Newcastle-on-Tyne in the north of England. These stones are the most siliceous of the three classes. The rock is characterized by uniformity of texture, keenness of "bite," and compactness. The fine-grained varieties are in great demand for edge tools and glass beveling. For the latter purpose they are to some extent exported to America.

The principal producing centers are Springwell, Sheriff Hill, and Gateshead. Some of the largest and oldest quarries at Springwell, 3 miles from Newcastle, formerly owned by J. Elliot, were purchased during the latter part of 1924 by Richard Kell & Co., Ltd. These quarries are

stated to be among the best in the country for grindstones and pulpstones. Grindstones from 1 to 6 ft. or more in diameter are produced.

Derbyshire or Peak stones, which are coarse sandstones, are largely used for pulpstones. They are obtained from the Millstone grits, especially the Lower or Kinderscout grit. However, grindstones suitable for

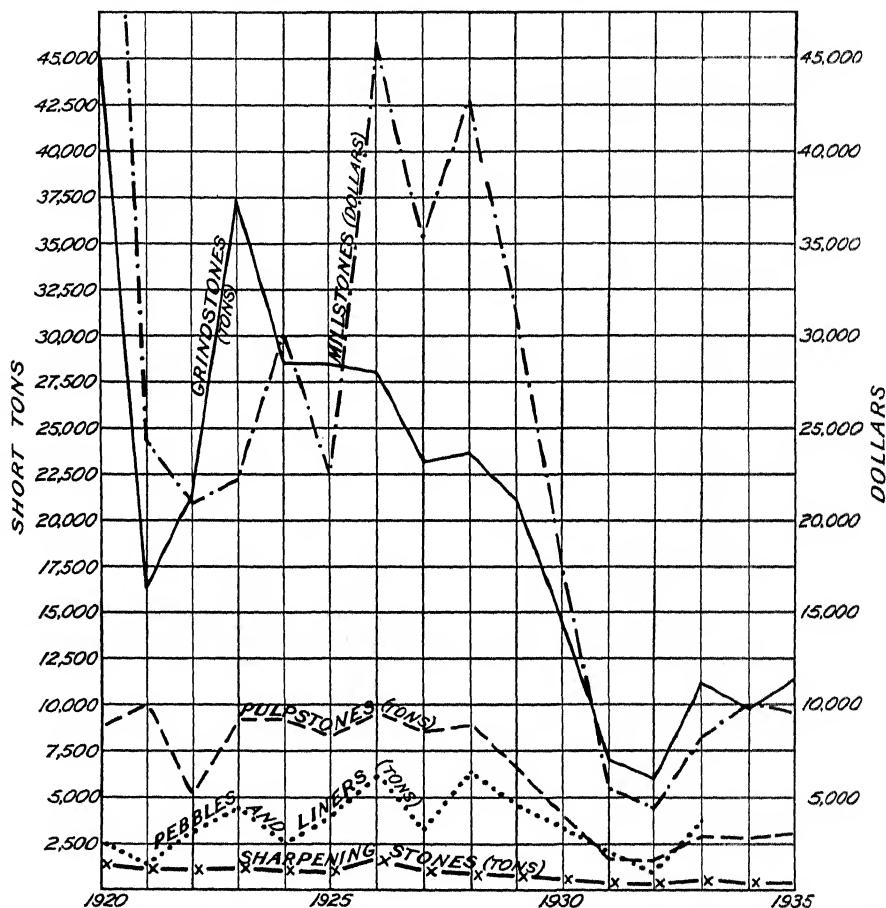


FIG. 4.—UNITED STATES PRODUCTION OF GRINDSTONES, PULPSTONES, SHARPENING STONES AND PEBBLES AND LINERS (TONS) AND MILLSTONES (DOLLARS), 1920-1935.

heavy work, such as grinding locomotive and heavy textile-machine parts, heavy edge tools, etc., are made from the coarsest Derbyshire stones. The principal producing centers are Rowsley and Matlock; the principal producer is James Akeroyd and Sons.

Yorkshire stones, typified by the Ackworth stone, generally have finer and sharper grits than the Derbyshire stones. They are usually light brown or buff, rather soft, fine-grained, thickly bedded sandstones. The best stones are obtained from the top of the middle Coal Measures.

The stones are used for grinding cutlery, saws, and fine edge tools. The grindstones are chiefly quarried from near Leeds, Pontefract, Rotherham, Normanton, Wickersley, Sheffield and at Cross Hills, the last named quarry being operated by Lombard & Co., of Boston, Mass.

*Other Countries.*—Details of the grindstone deposits and industry of other countries are lacking, but stones are being produced in Germany, Norway, Belgium, Italy and other central European countries.

## PRODUCTION

### *United States*

The peak of production in the last 15-year period was in 1923; since then the output has steadily declined and is now almost one-third of that year (Fig. 4). Eight companies were active in 1936, the largest being the Constitution Stone Co. and the Cleveland Quarries Ltd. About 85 per cent of the total output of grindstones now comes from the Washington County quarries at Marietta and Constitution, Ohio.

### *World*

*Canada.*—The grindstone output in Canada dropped from 2262 tons in 1920 to 360 tons in 1936.

*Other Countries.*—Production records of the larger producing countries such as England, Germany and Norway are not available, while statistics from other countries combine both grindstones and pulpstones. Some production and export figures are given in the Annual Statistical Summaries of the Imperial Institute, London, England.

## SPECIFICATIONS

A sandstone suitable for grinding purposes must be of uniform hardness, possess a sharp and even grain, and be free from clay or other impurities. The hardness is important, for if the stone is too soft it wears away rapidly, causing coarse and uneven grinding; if it is too hard it glazes and cuts so slowly that it is useless. The grains of silica should be cemented together in such a manner as to have sufficient tenacity to impart the necessary strength to the stone but at the same time crumble away with sufficient rapidity when exposed to friction to prevent glazing, as well as to present continually fresh, sharp grains. The size of the grit determines the ultimate use of the stone, as the coarser the grit the faster will be the cutting, although the work will be rougher.

## PRESENT STATUS OF THE INDUSTRY

During the latter part of the last century the grindstone industry was at its height, but for the past two or three decades there has been a gradual decline in tonnage production, caused mainly by the use of artificial

grinding wheels, which, owing to their superior cutting qualities, uniformity, ease of manipulation, and all-round efficiency, have replaced the natural stone for most general purposes. Today, the demand is mainly for stones of over 5 ft. in diameter, a market that limits the production to deposits of large, thick, and uniform beds. It is very doubtful whether grindstones will ever recapture the market held by the artificial abrasives for not only the practical but also the personal element must be considered. Workmen do not like to use grindstones, on account of the dirt and danger accompanying their use. At present the main uses for these large stones are, in order of their importance, for saw, file, machine-knife, scythe and shear grinding, for harvesting machinery and in the diemaking industry.

### PULPSTONES

Pulpstones are made from sandstone having a somewhat similar texture to that used for grindstones. However, in rare instances the same quarry furnishes both kinds of stone, but always from different beds. Since the grinding face of the stone is at right angles to the bedding, the beds must be at least 3 ft. thick to make even the smallest pulpstones, and should be 10 ft., capable of yielding stones of 6 to 7-ft. face, which are now in the greater demand.

### DISTRIBUTION OF DEPOSITS

The remarks regarding sandstone deposits suitable for grindstones are even more exacting for pulpstones, mainly because of the scarcity of deposits containing beds thick and free from cracks and inclusions from which the large stones can be produced. The United States and England are the foremost producers of pulpstones.

#### *United States*

In the past, pulpstones were produced from the sandstones at Steubenville, Lyria, Lisbon, Marietta and East Liverpool in Ohio, as well as from West Virginia and from Washington State. At present pulpstone activities are almost entirely confined to the sandstone beds along the Monongalia River and all within a radius of 10 miles between Fairmont and Morgantown in Monongalia County in the northern part of West Virginia. The quarries are at Opekiska, Flaggy Meadow, Tice and Uffington, and are now being operated by five companies, the Smallwood-Low Stone Co., West Virginia Pulpstone Corporation and the Smallwood Stone Co. being among the largest. On the west coast operations have been conducted for some years at Wilkeson, Pierce County, Washington, by the Walker Cut Stone Co., which in 1933 was one of the largest shippers of pulpstones.

*World*

*Canada.*—The principal sandstone beds from which Canadian pulpstones have, until recently, been obtained are in New Brunswick, in the vicinity of Newcastle and Quarryville, Northumberland County, and near Sackville and Dorchester, Westmorland County. The sandstone is somewhat soft, and beds thick and compact enough to supply the large stones are scarce. The present output comes from the west coast, on Gabriola and Newcastle Islands, off the east coast of Vancouver Island, British Columbia. The sandstone is harder and the beds thicker than those of New Brunswick. For full details see Mines Branch report.<sup>25</sup>

*England.*—The principal districts from which pulpstones are obtained are the close-grained, micaceous, drab sandstones of Darley Dale and the mottled coarser grained "Stoke" sandstone of Grindlefors, both in Derbyshire. Other districts are the yellow-brown beds of the Upper Coal Measures of Newcastle and Gateshead in Northumberland; also the Keighly district in Yorkshire and the Bilston quarries in Staffordshire.

*Other Countries.*—Pulpstones come from Sweden and Germany but information is lacking.

## COMMERCIAL CONTROL

Canada and the United States are large consumers of pulpstones and their production and sales are controlled by the situation of the pulp and paper industry. Some of these stones are exported to the American continent from England but competition is not serious. On the other hand, competition is increasing from the manufactured pulpstone produced in the United States and Canada. These stones are made up of segments of bonded silicon carbide or the fused-alumina abrasives. Well over 700 of these manufactured pulpstones are now in use throughout the world, over one-third of which are employed in Canadian mills.

## PRODUCTION

The United States and Canada are the only countries in which records are published separating grindstones, pulpstones, sharpening stones, and others.

*United States*

Pulpstone production is maintained from Monongalia County, West Virginia and from Wilkerson, Washington. The peak year was 1921, when 10,030 tons (\$750,063) was produced. There was a steady drop between 1928 and 1932; the output then increased slightly but is still less than one-third that of 1921. The production is shown in the general chart, Fig. 4.



The total imports by the United States of grindstones and pulpstones (not separated) in 1936 were 728 tons (\$24,638), England supplying 646 tons and Germany the remainder, against 534 tons (\$20,895) in 1935. The exports of these stones were 2480 tons (\$140,614) against 2764 tons (\$149,610) in 1935, of which in 1936 Canada took 90 per cent of the tonnage and 81 per cent of the value. Newfoundland took 1.5 per cent of the value. The remainder of the exports were principally small grindstones that went to 40 other countries, chiefly Mexico, South American countries and the West Indies.

*Canada.*—Pulpstones have been produced in Canada since 1892 and until 1923 all were from New Brunswick, the annual output ranging between 40 and 547 tons. In later years pulpstones have been obtained mainly from British Columbia. The peak production has been 1155 tons in 1926 and 911 tons in 1927; 266 tons in 1935 and 87 tons in 1936.

### QUARRYING AND PREPARATION FOR MARKET

The flat bed of the rock from which the stone is to be made is cut out to the required dimensions, after which the block is removed, placed in a gang saw and cut to the approximate thickness. The squared block is then placed under circular saws; the external diameter is cut to within  $\frac{1}{2}$  in. of the required dimensions and the center hole is cut out by a small saw, after which the stone is sent to a semiautomatic finishing machine, which cuts the face and sides accurately. After the stone has been inspected the hole is bored out to the required shape and size, and the edges of the face are beveled to guard against accidental chipping.

The method employed by one of the largest pulpstone producers in the United States is as follows: The corners of the cubical block are broken off by means of small air hammers and the stone is worked into a more cylindrical shape by means of the same tool, the top face being roughly finished off. The stone is then turned over and the other face worked in the same way, after which the whole stone is gone over carefully with the air hammer. The eye is made by drilling nine holes through the center and reaming them out with an air hammer. It is then finally squared for mounting on the lathe shaft. For finishing, the stone is lined up in the square shaft and held in position by wedges, one end of the shaft being free and unsupported so that the stone can be quickly and easily removed. Finishing operations are similar to those already described under grindstones, the turning tool being a 6-ft. bar fitted with a forged drill-steel bit. The stone is made to revolve about 20 r.p.m. and each bit is renewed after 8 to 10 revolutions of the stone. The sides of the stone are finished first, then the face, and finally the corners, and after removal from the table the center hole is finished by air hammers using tools of different lengths.

In the quarry at Gabriola Island, Nanaimo, B. C., the stones are cut in place, by means of circular steel cylinders of exactly the same internal diameter as the finished pulpstones, and about 1 ft. longer. Each cutter is rotated on its vertical axis and is pushed downward by an automatic feeder, which regulates the rate of boring to about 2 ft. per hour (for a 64-in. by 6-ft. cylinder). Split steel shot is used as the cutting medium. The whole machine is mounted on wheels in a wooden frame, so that it can travel on rails on the wide benches of the rock. The surface of the rock immediately under the cutting edge is leveled with plaster of Paris before operations are begun. The stone cylinders are freed by drilling a number of small horizontal holes at the bottom of the bench and splitting by means of light charges of powder. They are then lifted by derrick, loaded into barges, and shipped to the McDonald Stone Co. at Vancouver, where the center holes are bored and the stones cut to the required length. It is claimed that the advantages over the cubical-block method are minimum waste of good stone, a saving of labor in trimming, and a considerable saving in freight charges.

### SEASONING

The proper seasoning of pulpstones is of the utmost importance. The freshly quarried stone is saturated with water, which takes a considerable time to evaporate. As the moisture passes through the pores of the stone a process of cementation takes place, which forms a hard binder as the stone dries out. The finer the grit and the larger the stone, the longer the time required for drying out. The smaller stones should be seasoned for one year and the larger ones for about two years. In a poorly seasoned stone the cementation is not complete, the binder is soft and only the outside is hardened, consequently after a short time in operation the stone wears away rapidly or even fractures under the strain. The tying up of capital resulting from the stocking of a variety of stones valued at \$200 to \$1000 each presents a serious problem, and because of lack of capital, or rush orders, the length of proper seasoning is often not as long as it should be. Many experiments have been tried to shorten this period of seasoning by artificial means, but none appear to have been a real success. Among these is a process by which the stone is soaked in molten sulphur and allowed to cool, whereby the crushing strength is increased from two to three times the original. Although this is advantageous when the stone is to be used for building purposes, it does not appear to be successful for pulpstones. Another method of hastening seasoning is to steam-heat the stones to about 180° F. in a closed chamber for several hours and then allow them to cool slowly and age for about two months.

### SPECIFICATIONS AND TESTS

*Specifications.*—A good pulpstone should cut fast, produce fibers neither too coarse nor too fine, be of medium hardness, have a long life,

wear evenly, and withstand the strain. In order to produce the long, thin fibers the stone should tear and not cut, hence sandstones composed of subangular grains are desirable. If the grains are too rounded there is a tendency for the stone to glaze, thus producing inferior fiber. Coarse-grained stones cut faster than finer grained, but the pulp from the former is coarse and of poorer quality. The bonding material holding the grains together should be soft enough to wear away so as to leave the harder silica grains protruding. The stone should be uniform throughout, otherwise it will wear unevenly. If too hard it is liable to glaze and require too frequent regrinding of the face; if too soft it wears away too quickly. The ideal pulpstone must give a satisfactory number of grinding hours under severe conditions; high daily production; long life—that is, installations must be kept low—and be of a quality that makes unnecessary too frequent dressing or “jigging” of the stone.

Sandstone deposits having beds of the requisite thickness and physical qualities are rare.

At one time pulpstones of 26 or 27-in. face and 54 in. in diameter were mainly used, but in the modern large mills the demand is for magazine grinders of 54 to 62-in. face.

*Tests.*—Although the small-scale tests on certain sandstones, to determine their suitability for the manufacture of pulpstones, do not duplicate the actual conditions in the mill, a comparison with standard pulpstones of good quality indicates to a large degree the suitability of the sandstone under trial.

Details of tests and results are given in the Canadian Mines Branch report,<sup>25</sup> but, briefly, these tests constitute granulometric analysis in which the sandstone sample is carefully broken down to its natural grain and the fineness ascertained by screening. The hardness is determined by grinding cores of the stone on a horizontally revolving plate upon which quartz sand is fed. The toughness is ascertained by subjecting the cores to an impact machine of the Page type and the height required by a pointed weight to crack the test piece is measured. The structure and nature of the grain and bond are determined by the microscope and also chemically.

## MARKETING, USES AND PRICES

*Uses.*—Pulpstones are used for the production of wood fibers for papermaking. The previously cut short lengths varying from 2 to 4 ft. of barked wood are fed into a wood-grinding machine, where they are pressed by hydraulic pressure against the rotating face of the pulpstone.

*Marketing.*—In order to preserve the life and efficiency and obtain the full benefit of a pulpstone, it is necessary to treat it with care from the time it is cut out of the solid rock until it is finally discarded from the pulp mill. Great care must be exercised to prevent chipping of the face edges when handled by the cranes or if rolled over an uneven surface. It should be

crated for shipment and every endeavor should be made to eliminate the possibility of moisture and frost getting into the stone during transportation in winter. Whole carloads have not infrequently been ruined by neglect of the latter precaution. The rough handling of stones in quarry or transport often gives rise to the formation of fissures, which are the main causes of the breaking of a stone during operations.

*Prices.*—The values of shipments of all pulpstones from United States quarries averaged \$63 per ton for the past five years, the annual variations being from \$48 to \$83 per ton. In Canada there are almost 60 pulp mills using about 1000 stones valued at about one-half million dollars. The average value at the mills for the small stones for 2-ft. wood is \$300 each (2 to 2½ tons per stone); for 2½-ft. wood, \$335 each (3 to 4 tons per stone), and for 4-ft. wood, \$1100 (5½ to 7 tons per stone).

### SHARPENING STONES

These small hand-operated stones include scythestones, whetstones, honestones, razor hones, oilstones, waterstones, holystones or rubbing stones. Their nomenclature is somewhat confusing, as the difference between these stones is not clearly marked and they grade from one into the other according to texture and hardness.

*Scythestones.*—This division, as its name implies, constitutes all stones used for sharpening scythes and sickles. The grit is also suitable for kitchen and butcher knives and similar articles. They are the coarsest of the whetstones and are usually made from the finer beds of sandstone from which grindstones are obtained. The better grades of scythestone are usually fine-grained, highly siliceous argillite or mica schist, which in many cases contain, in addition to the quartz, innumerable minute crystals of some hard mineral such as garnet or magnetite.

*Razor Hones.*—Razor hones embrace all stones used for sharpening razors and delicate instruments. At present razor hones are largely made from artificial abrasives, although there is still quite a demand for the natural Belgian honestone.

*Oilstones.*—These stones, as the name indicates, are those very fine grit stones from which the most satisfactory service is obtained by the use of oil. There is a big demand for artificial oilstones, although large quantities of the opalescent, siliceous novaculite from Arkansas are annually used.

*Waterstones.*—Water is used with these stones, although very satisfactory results are obtained with oil. The best varieties are the Hindostan stone from Indiana and the Queer Creek stone from Ohio.

*Holystones or Rubbing Stones.*—These stones, which are made from blocks of close-grained sandstone, were at one time extensively used for rubbing down ships' decks and the name "holystones" is said to have originated from the fact that the work was done in a kneeling position.

The stones are now used to some extent for rubbing down rough surfaces on which a fine finish is to be applied, particularly automobile bodies, furniture and concrete work.

## DISTRIBUTION OF DEPOSITS

### *United States*

Sharpening stones have been quarried and manufactured for many years in various parts of the United States. The following varieties are produced and are described under the type of rocks.

*Novaculite*.—Novaculite is a fine-grained and compact white, quartzose rock, supposed to be a consolidated siliceous slime. It consists almost entirely of chalcedonic silica (over 99 per cent) and is of sedimentary origin. The rock is quarried principally from the vicinity of Hot Springs, Garland County, Arkansas. There are two varieties, the true novaculite (Arkansas stone) which is white, and the Washita (Ouachita) stone, which in many instances has a yellowish or rusty red tint.

ARKANSAS STONE is very dense and has a conchoidal fracture and waxy luster. It occurs in massive beds a few inches to 15 ft. thick, in the novaculite formation, which has a total thickness of 500 ft. and includes thin layers of shales and sandstones. As a result of pressure, the brittle novaculite has in many places been crushed and split; and, in addition, many fine quartz veins intersect the rock in all directions, some so thin as to be invisible to the naked eye. As these are detrimental, careful sorting is necessary, and the amount of waste is out of all proportion to the material eventually used. Large blocks of even apparently pure stone are not shipped, but are broken into pieces weighing up to 5 lb. Freezing also has an injurious effect on this stone, as its denseness does not allow for expansion. The Arkansas stone, which is produced in "hard" or "soft" grades, is especially suitable for sharpening fine-edged instruments and small tools and is used mainly by surgeons, dentists, engravers, jewellers, et cetera.

WASHITA STONE has approximately the same composition as the Arkansas but is less dense and more porous, has a subconchoidal fracture and resembles unglazed porcelain. It is freer from defects than the Arkansas stone; quartz veins are not so numerous, but cavities or "sand holes" are much more common. On account of its greater porosity, freezing does not have an injurious effect. Long drying is inadvisable, however, as it seems to cause loss of easy fracture and to make the stone tough and hard. The stone is less expensive than the Arkansas and is a faster cutting stone, but is used for coarser work. The Washita stone is shipped in blocks weighing 50 to 1000 lb. It is found in much larger quantity than the Arkansas stone and the demand for it is also much

greater. It is claimed that these novaculites give a much smoother and longer lasting edge than do the artificial stones.

*Mica Schist.*—Fine-grained, dark gray, highly siliceous, laminated mica schist is quarried at Pike, Grafton County, N. H. The quartz grains occur in definite layers separated by thin layers of mica. The part of the rock containing coarse, irregularly scattered quartz and argillaceous matter is discarded. There is a regular system of cross-jointing at right angles to the bedding planes, so that after blasting slabs or "bents" are easily pried out. The irregular slabs are first roughly trimmed, then further reduced and stacked. The Pike quarries have been producing scythestones for over a hundred years.

At Lisbon, also in Grafton County, the Pike company at one time produced the "chocolate" stone from a bluish chocolate colored schist. The demand for this stone has died out, so that quarrying for a few weeks provides enough for several years. It is used mainly by fishermen along the coast. In a quarry at Evansville, Orleans County, Vt., the rock is of a more massive formation than the Pike, and does not occur in layers.

*Sandstone.*—Among the better known is the Hindostan, or Orange stone, from French Lick and Northwest Township, Orange County, Indiana. Some of the crude material is shipped to Pike or Littleton for manufacture. It is a fairly soft, fine-grained, low-priced waterstone used mainly by mechanics and for domestic service. West Baden, Ind., is also a producing center.

Scythestones have been manufactured by several of the Ohio grindstone companies, particularly from the Berea and Euclid grits. The Queer Creek stone is a hard, dark gray, medium coarse sandstone, which is used as a waterstone for coarse sharpening. The Euclid is a blue, very fine grit stone used mainly for butcher and pocket knives. The Berea grits are used for the coarsest work, and the Huron for medium.

The Deerlick stone at Chagvin Falls, Cuyahoga County, Ohio, and the Labrador stone, which is somewhat similar to the Ohio sandstones, near Labrador Lake, Cortland County, New York, were at one time quarried to a small extent.

**RUBBING STONES.**—There are a number of sandstones of various grits, known as brown, blue, and red, that are extensively used for honing or rubbing marble or granite by hand. Other types of compact micaceous stone used for this purpose are the American Black Hone, and the Kentucky Caron Hone from Louisville and from West Baden, Indiana.

*Operators.*—During 1936 there were ten operators. The Norton-Pike Co. (the Pike Manufacturing Co. and the Norton Company amalgamated in 1933) being by far the largest. It produces scythestones from the schists of Pike, N. H., and Evansville, Orleans County, Vt., and also oilstones from the novaculite at Hot Springs, Ark., mined under contract. During the year scythestones were also made from the sandstone at

Berea, Ohio, and at West Baden, Ind., also rubbing stones from the latter district.

*Artificial Stone.*—Artificial sharpening stone made up of bonded fused alumina or silicon carbide fine grit is becoming more in demand than natural stone because of its faster cutting. It is probable, however, that there will always be a demand for natural novaculite oilstone for tools requiring a very keen edge, and for sandstone products for tools requiring a coarse, rough edge.

### *World*

*Canada.*—There are many fine-grained sandstones, siliceous argillites and mica schists in Canada that are suitable for sharpening stones, particularly in the Eastern Townships of Quebec; in Cumberland and Pictou Counties, Nova Scotia, and at Chaleur Bay, New Brunswick. A small output is maintained for fine-grained, blue-gray sandstone at Stonehaven, on Chaleur Bay, and from Shediac, Westmorland County, N. B.

*United Kingdom.*—Scythestones and honestones are made from the finer-grained sandstones of Bilston, Newcastle and from several parts of Yorkshire. A fine-grained micaceous sandstone from Talacre, Flintshire, is used for scythestones.

The most important kind of whetstone is the Scotch hone, sometimes called Water-of-Ayr, Snakstone, or Tam O'Shanter, obtained from Bridge of Stair, near Dalmore, Ayrshire, Scotland. It is a mottled, pale gray, very compact, Carboniferous shale and is used as an ordinary whetstone, also for a lithographic stone and for burnishing pulpstones.

Another good hone is the Charley Forest or Whittle Hill stone from Leicestershire, an exceedingly fine-grained, hard tuff from the Blackbrook series. The Idwal or Welsh oilstone, and the Cutler's Green from Snowden, Wales, have also been extensively used. The so-called "rag-stones" obtained from Scotland, and elsewhere, consist of siliceous mica schists having a twist along their length which gives a sharp "bite."

*Belgium.*—The well-known Belgian razor hone, sometimes called "soapstone" or "petrified woodstone," is a damourite slate containing innumerable garnets. The stone occurs in the form of 2 to 3-in., white to yellowish bands in a blue-gray slate (phyllade). As the slate has abrasive qualities also, the stones are usually double-faced, with the yellow damourite on one side and the gray slate on the other. These hones are quarried at Lierraux, Salm-Chateau, Bihau Sart, and Recht, in the Belgian Ardennes.

*Germany.*—The German water hone from Sonneberg is a hard, fine-grained, bluish green argillaceous schist. The Ratisbon hone, which is similar to the Belgian stone described above, occurs as a yellowish band from 1 to 18 in. wide in a blue slate.



*Asiatic Turkey.*—The oilstone from Smyrna, in Asia Minor, is in nearly all respects similar to the Arkansas novaculite, but it is not so uniform. It is, however, drab in color and carries an appreciable amount of free calcium carbonate and other impurities. Before the discovery of the Arkansas stone, it was regarded for several centuries as the best oilstone for mechanical tools.

*Other Countries.*—Whetstones are also made in Bavaria, Italy, Sweden, France and Japan.

### PRODUCTION

*United States.*—The present sources of supply are briefly reviewed under Distribution of Deposits. Statistics are given in Fig. 4. The peak of production during the past 15 years was 1680 tons (\$223,359) in 1926, but in the past five years production has been under 600 tons, the 1936 output being 752 tons (\$121,196). During 1935 some competition was felt from imports of natural sharpening stones, which amounted to 101 tons (\$53,563), of which 47 tons (\$4052) were from Germany; 24 tons (\$40,679 from Great Britain and 17 tons (\$1241) from Japan.

*Canada.*—From 50 to 100 years ago the output of these stones was substantial, but for the past 15 years the annual production has ranged between 17 and 169 tons, the 1936 output being 129 tons (\$4872). The low value is because the material from Shediac, N. B. is shipped in crude blocks to a United States manufacturer for finishing.

*Other Countries.*—Statistics of most of the other producing countries are not published separately, though France recorded 1120 long tons in 1928; 3320 tons in 1929 and 200 tons in 1932; Italy's records, however, from 1928 to 1933 show the following: 1796, 2377, 1568, 1500, 1250 and 1401 long tons of sharpening stones and whetstones.

### PREPARATIONS FOR MARKET AND USES

*Scythestones.*—For the making of scythestones from the fine-grained, siliceous schists of New Hampshire and Vermont, the rough slabs or "timbers" of the selected material are split at the quarry by means of knives and hammers, into approximately the required shape. They are then conveyed to the mill and placed on the rubbing beds, where they are ground to a uniform size. They are reversed until the required thickness is obtained, then are done up in bundles of 50 and the ends are trimmed to the required length. Each stone is finished separately by hand on the bed, the edges and ends being beveled. They are finally smoothed off by hand by means of a piece of hard stone, then are labeled and packed in boxes. Local sand is used as the abrasive to grind the stones and is fed to the bed by means of a Frenier pump.

*Arkansas Oilstones.*—The Arkansas novaculite from Hot Springs and the more porous Washita stone come from the mines in relatively



small lumps. The lumps are built up in layers into a large block, using plaster of Paris as the cement. When dry, the whole mass is sawed vertically by band saws into 2-in. slabs, after which the block is then sawed in a horizontal direction. The separate long strips are laid flat and again built up into a block with plaster and cut by the saws to the required length of about 8 in. The finishing is done by laying the pieces, after they are freed from the plaster, on the revolving face of a horizontal iron wheel, 5 to 6 ft. in diameter, using sand as the abrasive. The water absorbed by the Washita stone during the sawing or rubbing processes gives it a bluish green color, which is considered objectionable, so that after drying the stones are rubbed or "cleaned" with pumice to restore the original white.

The discards and small slabs resulting from the sawing operations are set evenly with plaster of Paris on the face of a small disk, which is placed face downwards and rests on the rubbing wheel. There are four of these disks to one wheel. Both the rubbing wheel and the disks containing the cemented stones revolve, resulting in a double grinding action. The process is repeated for the reverse side and for the ends. These disks and the small odd pieces are made up into the numerous forms and shapes requisite for the trade. Thin disks of novaculite used by jewelers, dentists, etc., are cut by diamond-toothed cylinders. Any other pieces that are not made up are ground into a powder and used by makers of watches and razor blades for polishing and grinding.

*Manufactured Sharpening Stones.*—For some purposes sharpening stones are made up artificially from a mixture of natural grits, such as a fine sand, crushed siliceous schist, and a clay bond. The ingredients in certain proportions and size of grit are thoroughly mixed together with water and silicate of soda, pressed into various shaped molds and baked. A typical stone of this kind is fitted with a handle and used for domestic sharpening of knives.

*Uses.*—The uses for sharpening stones are indicated under the description of the rocks from which they are made, the sharpening of coarse, medium or fine-edged tools being governed by the type and texture of the stone.

## MILLSTONES

The term "millstone," which includes the true burrstone and the chaser stone, is somewhat loosely applied to include circular stones revolved on a horizontal plane as well as those run on edge. They may be made from any hard and suitable rock varying from a sandstone, basalt, granite, to a quartz conglomerate. The true burrstone is a white to gray or slightly yellowish form of chalcedonic silica. The stone has a coarse, cellular structure, the holes being frequently due to the dissolving out of calcareous fossils. It has about the same hardness as flint, but is

not so brittle and possesses a straight fracture. Its sharp cutting power is due to the toughness of the rock and its numerous pores and cavities.

#### DISTRIBUTION OF DEPOSITS AND PRODUCTION

Rocks suitable for millstones occur in many countries and at one time the volume of trade in these stones was large. The United States, France, Sweden, Greece, Turkey, Yugoslavia, Italy and several other European countries are manufacturing millstones from beds of different kinds of rocks.

*United States.*—About 40 or 50 years ago millstones valued at around \$100,000 were produced annually in the United States, but recently the output has been between \$5000 and \$10,000 (Fig. 4).

Millstones have been produced from a fine-grained quartzite at Brush Mountain, Montgomery County, Virginia; from a quartz conglomerate at Parkwood, Moore County, and from a granite at Faith in Rowan County, both in North Carolina; from a quartz conglomerate, Lancaster County, Pennsylvania; from the Dutton sandstones of Jackson County; from a quartz conglomerate of similar texture to the Esopus stone, near Fair Haven, Rutland County, Vt.; and from a white variety of the Berea sandstone at Peninsula, Summit County, Ohio.<sup>26</sup> They are now made from the Shawangunk quartz conglomerate by four operators at Accord, two at Kerhonkson, and one at High Falls, Ulster County, N. Y.; one at Salisbury, Rowan County, N. C.; one at Cambria and one at Blacksburg, Montgomery County, Va. Import of millstones into the United States is very small; that in 1936 was 22 tons (\$2228), all from France.

*Canada.*—When the consumption of millstones was heavy, some 40 or 50 years ago, they were produced from Millstone Island, near the south-east extremity of Guysborough County, Nova Scotia, also from the Chaudiere River, Quebec; from north of the Cascades; at Murray Bay, Quebec and from near Cayuga, Ontario. It is, however, over 30 years since any millstones were produced in Canada.

*France.*—Some of the best burrstone is produced in France. It is a fresh-water, cellular quartzite or flint of Tertiary age, having great strength and toughness. The best stone comes from the top of the lower Oligocene of the Paris Basin, from a bed called the "Calcaire de Brie," which stretches from Vernon to Rheims and from Laon to Fontainebleau. The principal quarries are at La Fertesous-Jouarre. The stone occurs in large masses and is worked in open quarries and usually sold in irregular blocks. The blocks are shaped to the required dimensions and sold as solid stones, or else fitted together and bonded into solid wheels. The stone finds markets all over the world, and in 1922 about 434,000 short tons of burrstones and millstones was produced, but in 1932 this had dwindled to 23,200 tons.

*Germany.*—Millstones are produced from several localities in Germany, the principal one being at Andernach, 10 miles northwest of Coblenz, where the Niedermendig stone is mined. This is a porous trachyte-tuff. Other millstones are obtained from porous rhyolites found in the Odenwald, Thuringia, and the Fichtelgebirge district. The Ziltan millstone is a coarse conglomerate in a sandy matrix obtained from south-east Saxony.

*Other Countries.*—The number of stones produced in Belgium in 1929 was 141,700 and in 1933 was 51,010. The number in Greece was 1893 in 1929 and 4232 in 1933, and Turkey during the same years produced 2740 and 2768 millstones, respectively.

### CHASER STONES

Chaser stones are large, circular stones, run on edge, usually in pans paved with blocks of conglomerate or some hard material, and are used mainly for grinding minerals, chiefly feldspar, quartz and barites. They are made from a rock similar to those from which millstones are produced, but being larger are used for heavier work.

In the English chaser mills used for grinding spices, both Cornish and Aberdeen granites are employed; probably many other local igneous rocks could be so used, but lately it has been found more economical to import Italian granite for this purpose. In the Staffordshire potteries, two distinct varieties of chert were employed in grinding mills, the lower stone being a chert obtained from the base of the Millstone grit at Halkin Mountain, Flintshire, Wales. The upper was a cherty limestone obtained from Bakewell and Longstone Edge, Derbyshire.

### GRINDING PEBBLES AND TUBE-MILL LINERS

Extremely hard pebbles of flint or quartzite were used at one time to a large extent in cylindrical or conical mills for the grinding of cement, ores, paint, soft minerals, clays, etc. Steel balls and steel or rubber liners have to a large extent replaced the natural products, except where there may be danger of iron contamination from metal worn off the balls or liners. On this account the pottery industry is now probably the largest consumer of natural pebbles and liners.

In the United States the largest producer of both pebbles and liners is the Jasper Stone Co., Sioux City, Iowa. Small cubes or blocks are cut from the quartzite at Jasper, Minn., and artificially rounded by tumbling in rotating cylinders. Liners are cut from the same rock. These pebbles and liners are used for grinding cement, ores, silica, paint, gypsum, feldspar and in the ceramic industry. A few car lots of beach pebbles are shipped annually from Encinitas Beach, near Carlsbad, San Diego, Calif. These pebbles of granite, porphyry and quartzite are continually being carried ashore by means of floating kelp plants, to which they are

attached. The production in the United States during the past 15 years has ranged between 2000 and 6300 tons, except for the low year of 1932, when only 976 tons was sold (Fig. 4). The average value is about \$13 per ton.

In Canada, granite pebbles used for clinker grinding and in cement mills were at one time produced from the vicinity of Santoy, near Jackfish, on the north shore of Lake Superior, but none have been shipped for the past few years. Other localities are at Hedley, B. C.; Gabarus Bay, Cape Breton County, Nova Scotia, and in the Cypress hills of Saskatchewan.

The best known flint pebbles are obtained from deposits in Denmark, Belgium, and from the sea coast of France between Havre and St. Valéry-sur-Somme. Danish pebbles are recognized as the standard, because of their great hardness and toughness.

Flint pebbles are also produced in England and Norway; and various types of grinding pebbles have been exported from Germany, Italy, Labrador, Newfoundland and Japan. Belgium and Sweden are the chief foreign sources of tube-mill liners.

Imports of these products into the United States in 1935 amounted to 7829 tons (\$66,727) of which about half were from Denmark and the remainder from France and from Belgium.

There are seven sizes of Danish pebbles, ranging from 1 to 8 in. in diameter, each size from No. 1 to No. 7 being about 1 in. larger than the preceding one.

### SILICA

Silica sand and quartz are reviewed in detail in chapter XII, so that only their abrasive uses and applications are given below.

*Silica Sand.*—Silica sand is extensively used for sandblasting purposes, for the initial grinding or surfacing of plate glass, and as a cutting medium for gang saws on stone.

For sandblasting the main centers of production in the United States are Ottawa, Ill., and Cape May, N. J. The Ottawa material occurs as a friable sandstone, which is broken down to its natural grain, washed, and screened. The grains are spherical, resembling miniature pearls when seen under the lens. The Cape May sand is subangular and uneven in shape, but larger grain sizes are obtainable, more so than with the Ottawa sand.

In Canada sandblast sand is obtained from the decomposed rock containing friable quartz and china clay at Lac Remi, north of Montreal, Que.; from a similar type of material near Smoky Falls, north of Lake Nipissing, 25 miles west of North Bay, Ontario; also from a friable quartzite at East Templeton, Que., a few miles northeast of Ottawa, Ont. The grain of the Canadian sands is sharp.

The ranges of grain size are approximately: No. 1, between 20 and 35 mesh for light work; No. 2 between 10 and 28 mesh; No. 3 between 6 and 10 and No. 4 between 4 and 8 mesh. The last two are used for the heavy cast-iron work and steelwork.

Pure, clean beach and river sands, or Illinois sand, are used for the preliminary or coarse surfacing of plate glass. The crushed sand is water-graded into a number of grades at the glass plants and fed to the surfacing machines. Approximately three tons of sand is required to surface one ton of plate glass.

Cutting sand, composed of sharp, solid, quartz grains, is used as the abrasive for sawing stone. It is usually ungraded and about equivalent to a No. 1 sandblasting sand.

Burnishing sand is a fine, rounded-grain silica sand and of uniform size between 65 and 100 mesh, used in rolling down and burnishing gold decorations on porcelain. Tests on sandblasting sands and an interesting discussion on round versus sharp grains are given in detail in L. H. Cole's report.<sup>24</sup>

*Quartz.*—Crushed and graded quartz is used for the abrasive backing of "flint" sandpapers. Almost any deposit of massive white quartz is suitable. Being the cheapest of all the abrasive-coated papers, it still is sold in fair amount, mainly in hardware stores and by small jobbers. It is made only in the form of paper, not as cloth. True chalk flint from England and France is extensively employed for this purpose in Europe and has better cutting qualities and longer life than ordinary quartz.

Powdered quartz and silt are sometimes used for scouring compounds and for the harsher metal polishes.

### SOFT SILICEOUS POWDER ABRASIVES

Many natural highly siliceous materials either occur as a powder or are used only in the powder form for mild abrasives. For the majority of these use as an abrasive is of minor importance as compared to their principal applications. Among these, diatomite, pumice and tripoli are reviewed elsewhere (chapters XIII, XXXV and XLVIII). Their abrasive uses are therefore only briefly given below.

*Pumice.*—Under this title are included lump pumice and pumicite or volcanic dust, the natural powder. Lump pumice is used by manufacturers of furniture and musical instruments for dressing the wood and metal surfaces; by silver platers for preparing their metal surfaces; by lithographers for cleaning the stone surfaces; for rubbing down and polishing fine tools and instruments and for domestic and toilet uses, such as hand cleaners. Pumicite or ground pumice is mainly used as a cleanser, the thin, sharp and striated grains being particularly suitable for this purpose. It is also made up in the form of hand soaps. During 1935, in

the United States, 50,640 tons valued at \$176,456, or 88 per cent of the total tonnage of pumice sales, was used for cleansing and scouring compounds and for hand soaps, and about 2 per cent for other abrasive uses, which include polishing compounds, polishing powders for bone, celluloid, and hard rubber, in dentists' tape and in some rubber erasers.

An artificial pumice used for abrasive purposes is made in Germany. In this process obsidian or volcanic glass preheated to 900° C. is dropped down a shaft furnace against a rising draft of hot gases. The obsidian swells into porous particles and is then consolidated with lime or cement to a form resembling a pumice, which has an apparent specific gravity of less than that of natural pumice.

*Tripoli, Microcrystalline Silica and Rottenstone.*—These fine-grained, porous materials are known to the trade as "soft silicas." Tripoli, which in the United States comes from southwest Missouri and northeast Oklahoma, is mainly used (about 70 per cent of tripoli production) in the form of made-up tripoli grease bricks or tripoli compositions for buffing and polishing. The compound is applied to a rapidly revolving belt or canvas wheel and used for the finishing or buffing of metals, plated products, etc. It is also used to a small extent in the manufacture of some scouring and cleaning powders and soaps; for the rubbing down of painted surfaces, such as automobile bodies. A similar but finer grained material occurring in the northwest corner of Arkansas, about 50 miles southeast of the Missouri deposits, is used mainly for oil-well drilling mud. Microcrystalline (sometimes erroneously termed "amorphous") silica, which comes mainly from southwestern Illinois, and to some extent from Wayne County, Tennessee, is also used as buffing and polishing compounds. These compounds are termed "silica" by the trade and are much in demand for white "coloring" operations on high-class work. Chemically precipitated amorphous silicas are also used in polishing and buffing compositions. Both tripoli and microcrystalline silica are mined from deposits at Harrisburg, northwestern Georgia. Rottenstone, a fine-grained gray-buff siliceous-argillaceous limestone, comes from Antes Forte, Lycoming County, Pa., and is used as a polish base; for instance, for automobile polishes. During 1936, in the United States, 16,443 tons valued at \$247,948, which was 59.8 per cent of the tonnage and 64.0 per cent of the value of the total sales of these three materials was used for abrasive purposes, mainly in grease compositions.

*Diatomite.*—Approximately 98 per cent of the diatomite (diatomaceous silica, kieselguhr, etc.) production in the United States comes from the Marine deposits of western California. The amount used for abrasives is insignificant in comparison to its other applications. As an abrasive it is mainly used in metal (silver) polishes, powders and pastes and in some automobile polishes, dental powders and pastes and occasionally as a friction agent in match heads or on the sides of boxes.

## NONSILICEOUS SOFT ABRASIVES

*Ground Feldspar* is employed to some extent in scouring and cleaning compounds and for a window cleaner.

*Lime*.—This so-called “Vienna” lime (originally from Vienna, Austria) that is used on the American continent in grease-brick buffing composition is obtained from certain beds of dolomite at Francis Creek and Manitowoc, Wis. Vienna lime is made by calcining the dolomite and cleaning and grinding to a certain fineness. It is packed in carefully sealed containers. As soon as the lime becomes hydrated it ceases to function and also attacks the grease compositions. It is used for the buffing of brass, copper, bronze, steel, pearl, celluloid, etc., but its main use is for the “coloring” of nickel after plating, as it gives it a deep “under surface” blue peculiar to the metal. Lime attacks aluminum, therefore it is not used on that metal.

*Chalk*.—Chalk (calcium carbonate) is a soft, compact, fine-grained, white limestone composed of the calcareous remains of small Marine shells. A small amount of this chalk—mainly from England and France—known as “whiting” is used as a very mild abrasive for hand-polishing of nickel, gold, silver or plate ware, buttons, et cetera.

*China Clay* (kaolin) and some pipe clays have been successfully used in polishing powders. Pipe clay was at one time the standard polish for naval and military tunic buttons.

*Talc* is used for polishing rice grains.

*Metallic Oxide Buffing Materials*.—As these are manufactured products, they are outside the sphere of this review. Briefly, they consist of various iron oxides such as crocus (red-brown), rouge (red), black rouge (magnetic iron oxide) mainly for glass, green rouge (chromium oxide) mainly for platinum and stainless steels; satin rouge (lampblack) for celluloid and bone; manganese dioxide; putty powder (tin oxide) for stone polishing.

## MANUFACTURED ABRASIVES

Manufactured or artificial abrasives are divided into four main groups: (1) silicon carbide (sold under the trade names Carborundum, Crystolon, Carbolon, etc.); (2) fused alumina (sold under the trade names Alundum, Aloxite, Lionite, etc.); (3) boron carbide (Norbide); (4) metallic abrasives such as steel shot and grit and steel wool, and various metallic oxides used in buffing and polishing compounds. As these are all manufactured materials, rather than natural mineral products, space is devoted to them only to the extent of showing the amounts in which they are used in competition with the natural abrasives. Details of their manufacture and uses are given in the Mines Branch publication.<sup>25</sup>

Silicon carbide is made by three companies having one plant in the United States and three plants in Canada. Fused-alumina abrasive is

made by six companies having two plants in the United States and five plants in Canada. The three manufacturers of silicon carbide make both products and are included in the fused-alumina list. There are also manufacturers of both products in France, Norway, Sweden, Germany and other European countries.

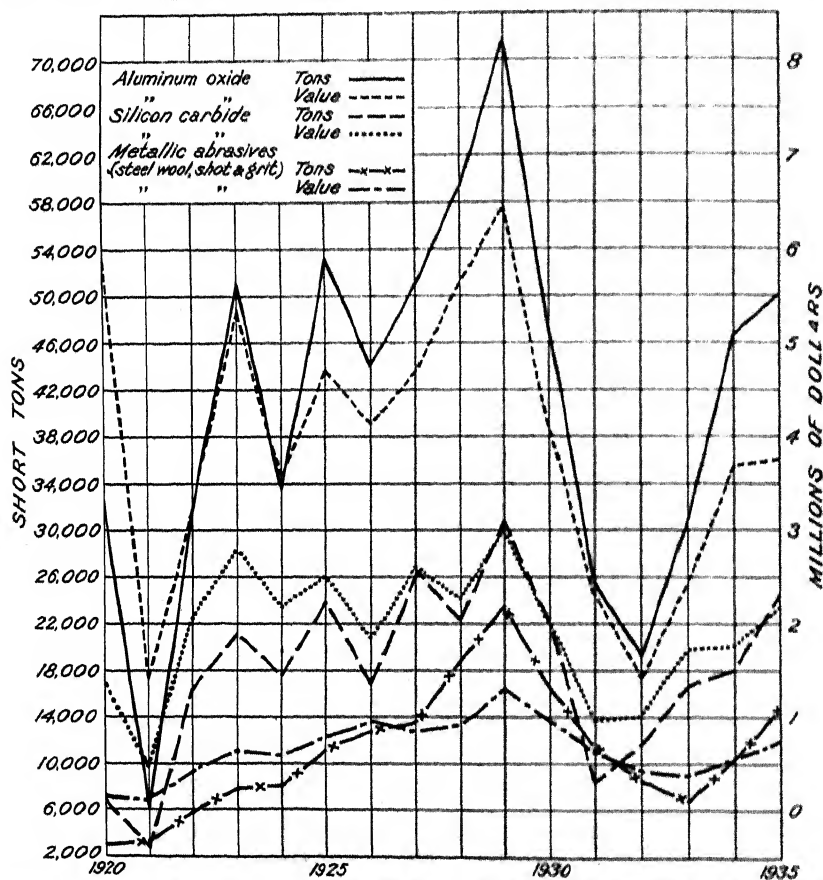


FIG. 5.—CRUDE MANUFACTURED ABRASIVES SOLD OR USED FROM PLANTS IN THE UNITED STATES AND CANADA, 1920-1935.

The new product Norbide (boron carbide) was produced by the Norton Company, Chippawa, Ont., Canada, in 1934. This product, harder than silicon carbide or fused alumina, is the hardest known manufactured material, very closely approaching the diamond. Its uses are now being developed, but at present its main outlet is in the form of molded products for sandblast nozzle liners, extrusion dies and for thread guides in textile machinery. The powder is used for many grinding and lapping operations that previously have been possible only with diamond dust. It is of interest to users of hard abrasives that the old Mohs' scale, in which quartz was 7, garnet 8, corundum (fused alumina) 9, and diamond 10,



has been extended to quartz 8, garnet 10, corundum and tungsten carbide both 12, silicon carbide 13, boron carbide 14, and diamond 15.

The large volume of business in recent years of these manufactured products is indicated by Fig. 5. In the peak year of 1929 the output from United States and Canada of silicon carbide, aluminum oxide and metallic abrasives amounted to 126,712 tons, valued at \$10,821,696, after which there was a substantial drop up to 1932, when the value was under three million dollars, and then a gradual rise to 123,834 tons (\$7,274,986) in 1936.

Approximately 95 to 98 per cent of the total imports into the United States of silicon carbide and fused-alumina abrasives are from Canada in the form of crude material made therein by companies of which the head offices and crushing and grading plants are in the United States. From 1000 to 1500 tons of the manufactured abrasives are imported annually from Europe and come from Norway, Germany, Sweden, Austria and France.

Details covering the manufacture of these abrasives, as well as the manufacture of grinding wheels, sandpaper, buffing compounds, etc., and their special industrial applications will be found in the Canadian Mines Branch report.<sup>25</sup>

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SILLIMANITE GROUP—ANDALUSITE, KYANITE,  
SILLIMANITE, DUMORTIERITE

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**R**EFRACTORIES as a whole are treated in a general chapter by Tyler and Heuer. In this and other chapters the special characteristics of individual minerals of particular importance in their field are discussed more in detail. Andalusite, kyanite, sillimanite and dumortierite† have in common the capacity to withstand high temperatures and to change over into mullite, and it is this that makes them useful as refractories.

The four minerals andalusite, kyanite, sillimanite and dumortierite may be considered as a group because of similar ceramic use. All are in demand for high-grade refractories. Porcelain produced from these minerals is valuable because of its high melting point, high insulating power when heated, low coefficient of expansion and resistance to the corrosive action of certain fluxing agencies and furnace gases.<sup>59†</sup> The minerals of this group toughen the product to which they are added and are favored in the manufacture of porcelain for spark plugs, refractory brick, electrical and chemical porcelain and chinaware, enamelware and hotelware. Refractories with these minerals as component parts are used in glasshouse refractories; crucible, boiler, brass-melting, electric and forging furnaces; high-temperature cements; oil and gas fireboxes; combustion tunnels and cement-kiln linings.

## COMPOSITION

The three aluminum silicates, andalusite, kyanite and sillimanite, have an  $\text{Al}_2\text{O}_3:\text{SiO}_2$  ratio of 1:1, but differ in crystallization. Andalusite and sillimanite are orthorhombic, but structurally different, while kyanite is triclinic. Dumortierite is a basic aluminum borosilicate,<sup>42,56</sup> approxi-

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† Synonyms or varieties:

Andalusite var. *chiastolite* is a type found in crystals having symmetrical black markings due to carbonaceous inclusions. *Viridine* contains iron and manganese (mangan-andalusite).

Sillimanite syn. *fibrolite* var. *monrolite*, *bamlite*, *xenolite* and *worthite*.

Kyanite syn. *cyanite*, *disthene*. (Committee on Nomenclature, Mineralogical Society of America has approved the spelling *kyanite*.)

‡ References are at the end of the chapter.

mately  $8\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$  and orthorhombic in crystallization. It is closely related in thermal behavior to the three aluminum silicates mentioned and has a corresponding practical application. The four minerals are converted above  $1545^\circ \text{C.}$  to an artificial product<sup>2</sup> having the composition  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and vitreous silica. The aluminum silicate,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , is generally referred to under the name mullite because of agreement with the rare mineral of that name. The vitreous silica is thought to be cristobalite.<sup>14</sup> In recent years outstanding contributions have been made to the understanding of the binary series alumina-silica.<sup>2,43</sup> Bowen and Greig have shown that the constituents resulting from the fusion of pure  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in all proportions and at temperatures up to  $2000^\circ \text{C.}$  are liquid, cristobalite, mullite and corundum (Fig. 1). The

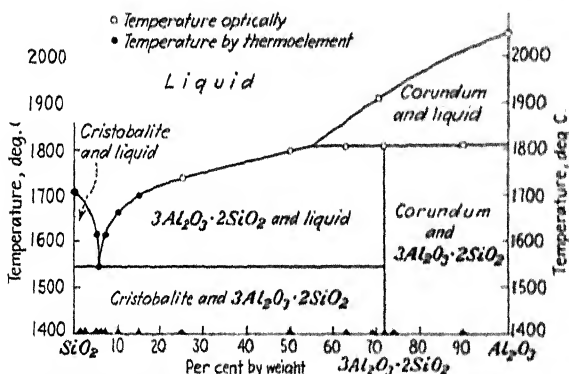


FIG. 1.—EQUILIBRIUM DIAGRAM OF THE SYSTEM  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ , AFTER BOWEN AND GREIG.

mixture 71.8 per cent  $\text{Al}_2\text{O}_3$  and 28.2 per cent  $\text{SiO}_2$  forms pure mullite, which is stable to  $1810^\circ \text{C.}$ ; above this temperature it forms corundum and liquid.<sup>3</sup> Mullite<sup>3</sup> is orthorhombic in crystallization with a slight but definite difference from sillimanite. This difference was not detected at first even with X-ray work,<sup>5,31,32,33,60</sup> and early descriptions refer to the artificial product secured by calcination of the aluminum minerals as "artificial sillimanite."

### PROPERTIES

The ordinary physical properties and the optical properties of the minerals belonging to this group are outlined in Table 2. The optical properties<sup>3,29</sup> are probably most used in identifying the minerals, and specific gravity is relied upon to a large degree in estimating commercial grades. The thermal properties of the minerals are of primary importance in determining their usefulness in industry. The utilization of all these minerals depends upon the inherent properties of mullite and the type of mullite crystals produced by calcination. Mullite is heat-resistant, is a good insulator even at high temperatures<sup>26</sup> and, perhaps

most important of all, is resistant to shock.<sup>41</sup> Mullite remains stable to a temperature of 1810° C. Above this temperature it does not break down completely but changes to corundum and liquid.

Dumortierite has a practical advantage over the other three in refractories because of its higher  $\text{Al}_2\text{O}_3$  content.<sup>4</sup> In general, for determining its refractory nature, dumortierite may be assumed to be  $4\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$  and the thermal behavior may be determined from the alumina-silica diagram. At 1545° C. the liquid formed is about 4 per cent, which is considerably less than with andalusite, kyanite or sillimanite (14 per cent). The small amount of liquid formed from dumortierite as contrasted with the other three has a favorable effect on the load characteristics<sup>4</sup> of the calcined product.

Natural sillimanite can be heated for long periods at any temperature below 1545° C., without changing,<sup>2</sup> although all evidence indicates that the 1:1 compound has no stable existence at high temperatures. Above 1545° C. sillimanite breaks up into  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and liquid. Sillimanite would be a desirable refractory if found in commercial quantities in accessible localities.

When any one of these four minerals changes to mullite, the new phases formed are of lower density than the original mineral. The expansion that results is negligible for andalusite and dumortierite, is slight for sillimanite and is considerable for kyanite.<sup>55</sup> Because of expansion on heating, kyanite may be used to advantage in combination with diaspore or bauxite in the preparation of refractories.<sup>13</sup> The expansion of kyanite will counteract the shrinkage of diaspore or bauxite.

Mullite is similar in optical properties to sillimanite, differing principally in refractive indices and axial angle.<sup>3</sup> The refractive indices of mullite may increase in value with  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  up to 4 per cent, when the values of  $\alpha$  and  $\gamma$  become virtually identical with normal sillimanite. In porcelain it usually forms fine needlelike crystals indistinguishable from sillimanite without optical determinations.

Since andalusite shows almost no volume change at dissociation, and kyanite shows great expansion and disintegration, treatment of the two minerals in ceramic practice differs greatly. Andalusite is usually molded into final form and fired directly<sup>40,41</sup> while kyanite is precalcined. The properties of the resulting porcelain may be as valuable in either case and the economic advantage of a more constant source of supply for kyanite may more than offset any advantage andalusite may have in requiring a single firing.

Kyanite, andalusite and sillimanite<sup>14</sup> have no definite temperature at which sharp decomposition occurs to form new phases; nor is there any considerable temperature below which the mineral remains unaffected for an indefinitely long period. In practice<sup>36</sup> kyanite breaks down at cone 12 (1350° C.) to mullite and glass, andalusite at cone 13 (1350° C.) and

sillimanite is not decomposed up to cone 15 (1435° C.). Kyanite and andalusite are decomposed with absorption of heat and yield mullite 87.64 per cent and silica 12.36 per cent.<sup>14</sup> Kyanite is more readily decomposed than andalusite.<sup>14,36</sup>

Measurements by X-ray, and crystal-structure determinations of andalusite, sillimanite and kyanite are fairly complete.<sup>6</sup> The unit cells and space groups of the natural forms of  $\text{Al}_2\text{SiO}_5$  are as shown in the table below.<sup>16,49,50,51,52,53,60</sup>

The unit cells for kyanite, sillimanite and andalusite each contain four molecules of the composition  $\text{Al}_2\text{SiO}_5$ . Mullite has a slight structural difference from sillimanite and shows a substitution of aluminum atoms for silicon atoms without any appreciable disturbance of the arrangement of the oxygen atoms. The unit cell for mullite has the dimensions:

$$a = 7.49 \text{ \AA.}, \quad b = 7.63 \text{ \AA.}, \quad c = 2.87 \text{ \AA.}$$

and the unit cell contains three-fourths of a molecule of  $\text{Al}_6\text{Si}_2\text{O}_{13}$ .

The electrical resistances of kyanite, sillimanite, andalusite and dumortierite have been determined by King<sup>26</sup> in ohms per cubic centimeter for fired material at various temperatures. Mullite derived from kyanite was found to have a better electrical resistance than mullite derived from any of the other members of the group.

TABLE 1.—*Structural Data*

	<i>a</i> , Å.	<i>b</i> , Å.	<i>c</i> , Å.	$\alpha$	$\beta$	$\gamma$
Kyanite:						
triclinic, <i>C</i> <sub>2</sub> ' .....	7.09	7.72	5.56	90° 5½'	101° 2'	105° 44½'
Sillimanite:						
orthorhombic, <i>V</i> <sub>A</sub> <sup>16</sup> .....	7.43	7.58	5.74			
Andalusite:						
orthorhombic, <i>V</i> <sub>A</sub> <sup>12</sup> .....	7.76	7.90	5.56			

## ORIGIN AND MODE OF OCCURRENCE

**Kyanite.**—Kyanite is a common mineral in areas of metamorphic rocks. It occurs in many places in the belt of crystalline rocks that traverses the states along the Atlantic seaboard of the United States. The mineral occurs: (1) in gneiss or schist in disseminated crystals, (2) as lenses in pegmatite dikes, (3) irregularly distributed through quartz veins or quartzitic masses, and (4) in residual clay formed by the weathering of kyanite gneiss. One of the most frequently associated minerals is quartz. The most important occurrences commercially are the deposits of disseminated crystals in gneiss or schist.

A disseminated deposit of considerable size is being worked at the extreme north end of Black Mountain Range, near Burnsville, N. C., in the Carolina gneiss (by Celo Mines Inc.). The deposit is cigar-shaped, 250 ft. wide by 2000 ft. long, and has been developed at one point with a vertical face of over 150 ft. exposed. It is reported to be steeply inclined (dip  $77^\circ$ ) and has been assumed to have continuity with depth. The kyanite occurs in coarse platy crystals usually an inch or less in length but occasionally more than two inches long. The plates are about  $\frac{1}{16}$  in. thick and vary from  $\frac{1}{4}$  to  $\frac{1}{2}$  in. in width. Commonly associated with the kyanite are quartz, feldspar, biotite, numerous minute crystals of garnet, some muscovite and iron sulphides. Other minerals are tourmaline, beryl and staurolite.

The small scattered lenses found in pegmatites, the kyanite in the gold-quartz veins and the kyanite in the quartzitic masses are of little commercial importance. Residual and placer kyanites are being mined in Georgia<sup>39</sup> in small amounts.

Kyanite is thought to be formed under great pressure and high temperature in the crystalline rocks as a result of metamorphism of aluminous members of a stratified series.<sup>20</sup> Difference of opinion exists concerning the presence or absence of accompanying magmatic activity. The absence of intrusives in the immediate vicinity of certain deposits is cited as evidence against magmatic influence.<sup>20</sup> However, Bayley, Keith, Watson and Taber have given evidence<sup>21, 22, 48, 57, 58, 1, 44</sup> of igneous activity in the region and intrusives occur even in certain kyanite areas. It is difficult under such circumstances to separate unmodified dynamothermal metamorphism from dynamothermal metamorphism accompanied by the penetrating influence of confined igneous emanations. The association of beryl and tourmaline with the kyanite is an indication of pneumatolytic activity.

In India kyanite occurs in quartz-kyanite or kyanite schist and is associated with muscovite schist.<sup>10</sup> The kyanite deposits of the Bhandara district in India are of the schistose type and, although of little commercial value, are of interest because of the genetic relations observed. Both kyanite and sillimanite occur in the district but are mutually exclusive of each other. It is believed<sup>7</sup> that chlorite-muscovite schists yielded the rocks bearing kyanite and sillimanite as the result of pneumatolytic and hydrothermal metamorphism attendant upon the intrusion of adjacent granite and involving the separation of boric oxide or borates and occasionally vanadates derived from its residual magma liquor. Genetic relationships of minerals such as dumortierite, tourmaline, roscoelite mica and rutile, associated mica schist and prominent quartz veins support this theory of origin.

*Andalusite.*—Andalusite occurs in argillaceous schists, slates, gneisses and phyllites, and in granite pegmatites. It is commonly associated

TABLE 2.—Physical and Optical Properties

Mineral	Crystal System	Specific Gravity	Hardness	Cleavage	Optics <sup>a</sup>					
					$\alpha$	$\beta$	$\gamma$	Sign	Angle	Orientation
Andalusite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ).....	Orthorhombic	3.16-3.20	7.5	{110} good	1.634	1.639	1.643	Bx -	$2V = 85^\circ$ $r > v$ faint	$X = c$ $Z = a$
Sillimanite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) .....	Orthorhombic	3.23-3.24	6-7	{010} perfect	1.659	1.660	1.680	Bx +	$2V = 25^\circ-30^\circ$ $r > v$ perc.	$X = b$ $Z = c$
Kyanite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) .....	Triclinic	3.56-3.67	Varies with direction	{100} perfect {010} good {001} parting	1.712	1.720	1.728	Bx -	$2V = 92^\circ$ $r > v$ slight	$X$ almost $\perp$ to {100} Ext. on {100} $Z \wedge c = -30^\circ \pm$
Dumortierite $8\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$ ).....	Orthorhombic	3.26-3.36	4-7	{100} good	1.678	1.686	1.689	Bx -	$2V = 30^\circ-40^\circ$ $r < v$	$X \wedge c = 0^\circ \pm$ $Z = a$
Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).....	Orthorhombic	3.156	6-7	{010} perfect	1.638	1.642	1.653	Bx +	$2V = 45^\circ-50^\circ$ $r > v$ perc.	$X = b$ $Z = c$

<sup>a</sup> Optical data are given by Larsen and Berman,<sup>22</sup> Peck,<sup>23</sup> Schaller,<sup>24</sup> Wright,<sup>25</sup> Bowen,<sup>2</sup> and Greig.<sup>14</sup>



with tourmaline, corundum, topaz, garnet, pyrophyllite, quartz, biotite and muscovite. The andalusite at White Mountain, Mono County, California, occurs in irregular segregations in a lenticular quartz mass, with a narrow thickness of sericite schist on either side. The deposit appears to have been produced by a sequence of metamorphic proc-

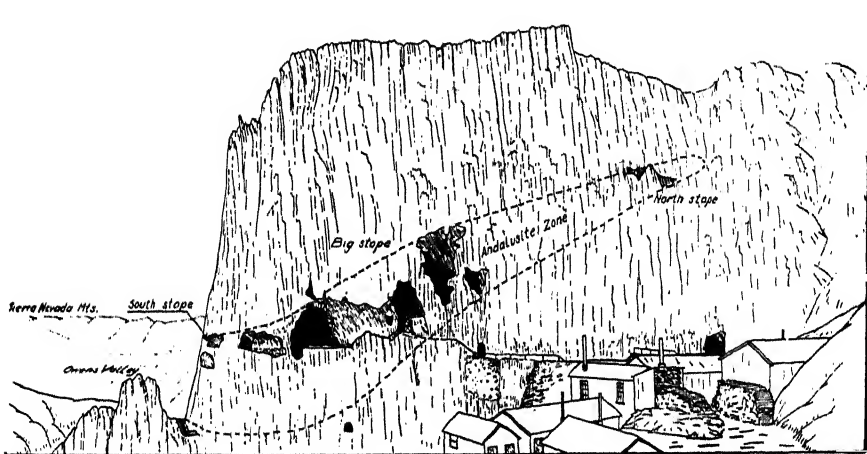


FIG. 2.—SKETCH ILLUSTRATING DISTRIBUTION OF ANDALUSITE IN QUARTZ MASS AT WHITE MOUNTAIN, CALIFORNIA. (*Econ. Geol.*, 1932, 27, 619.)

esses.<sup>11,23</sup> The original rock probably consisted of a series of trachytic flows with an intervening layer of aluminous volcanic material (or possibly an aluminous sediment). The andalusite was apparently



FIG. 3.

FIG. 4.

FIG. 3.—THIN SECTION OF ANDALUSITE CRYSTAL FROM WHITE MOUNTAIN, CALIFORNIA, SHOWING IRREGULAR QUARTZ AREAS SCATTERED THROUGH CRYSTAL.  $\times 10$ .

FIG. 4.—THIN SECTION OF ANDALUSITE FROM WHITE MOUNTAIN, CALIFORNIA. CROSSED NICOLS,  $\times 10$ .

produced by metamorphism of the original rock as one of the effects of an adjacent igneous intrusion.

The geologic features, wide distribution of titanium minerals throughout both the country rock and the andalusite mass, extensive tourmalini-

zation and inherited structures in the sericite schist, suggest pneumatolytic and later processes connected with an intrusive. It is thought that in the early stages of the formation of the deposit, metamorphism brought about the transfer of aluminous material from an aluminous rock to andalusite segregations bordering a quartz mass. The chief concentrations of andalusite have been found in the quartz not far from the mica schist. Tourmaline, topaz and diaspore, minerals indicative of igneous activity, were genetically related to the early mineralization. Abundantmiarolitic cavities in the deposit also indicate gaseous influence. In brief, the andalusite deposit at White Mountain is probably due to pneumatolytic metamorphic action along the contact between a quartzitic mass and aluminous layer, resulting from igneous influence. Hydrothermal metamorphism at a later stage is indicated by extensive pyrophyllitization and sericitization.

Andalusite occurs near Hawthorne, Mineral County, Nevada, associated with corundum and diaspore, in a vertical veinlike deposit, 2 to 4 ft. thick, approximately 3000 ft. long and with an explored depth of 100 ft.\*

*Dumortierite*.—Dumortierite is found in pegmatite or quartz veins, which cut aluminous rocks such as cordierite or corundum gneiss or mica schist, and has been observed in kaolinized products of a micaceous granite. At Oreana, Nev.,<sup>19,37</sup> dumortierite occurs near the border and within a quartz mass formed by pneumatolytic invasions of a rhyolitic tuff.<sup>24</sup> The quartz mass is associated with a sericite schist in which occur irregular lenses of andalusite, partially or entirely altered to dumortierite. In massive character, size and association with a mica schist, it is similar to the quartz segregation containing andalusite at White Mountain, California.

The series of metamorphosed Triassic volcanics in which dumortierite occurs is not far distant from a granite intrusive.<sup>18</sup> It is likely that the emanations from this intrusive or hidden intrusives of a similar nature have forced their way upward through the Triassic series, bringing about crystallization of the andalusite and later dumortierite by metamorphism along the boundaries of the quartz mass adjoining the mica schist. The earlier phase was probably pneumatolytic when andalusite and earlier dumortierite were formed. Later, presumably hydrothermal metamorphism resulted in the formation of late dumortierite. Three generations of dumortierite were produced: (1) coarse euhedral blue dumortierite frequently found in crystals (probably early), (2) mottled lavender or pink masses (the bulk of the commercial ore) and (3) fibrous pink veins or isolated crystals.

*Sillimanite*.—Sillimanite occurs in gneisses, schists, slates and hornfels, and is probably produced at higher temperatures in nature than the

\* Letter by Clifford Tillotson, Tillotson Clay Products Co., Los Angeles, Calif.

other minerals of the group, but under essentially similar conditions of metamorphism. It is found in separate crystals or in aggregations of slender minute prisms in radiating or diverse arrangement, often accompanied by garnet, cordierite, corundum, andalusite and rarely kyanite.<sup>7,39</sup> Important deposits occur in India<sup>10</sup> at Khasi Hills, Assam, and at Pipra, Rewa. At the latter place sillimanite is found in an area of sillimanite schist associated with corundum and surrounded by granitic gneiss. Both deposits are too inaccessible at present to be profitably mined.

*Mullite*.—Although common in refractories, mullite is rare in nature. In fact, it was only after identifying the aluminous silicate of refractories as  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  that Bowen and Greig found natural material of a similar composition in buchites described by Thomas.<sup>54</sup> The *buchites* are fused argillaceous sediments occurring rather frequently as inclusions in the Western Isles of Scotland<sup>14,45</sup> and were found to contain a product



FIG. 5.

FIG. 6.

FIG. 5.—THIN SECTION OF EUBEDRAL DUMORTIERITE CRYSTALS IN A QUARTZ SERICITE GROUNDMASS, OREANA, NEVADA.  $\times 10$ .

FIG. 6.—THIN SECTION OF SCATTERED CRYSTALS OF DUMORTIERITE IN QUARTZ SERICITE GROUNDMASS, OREANA, NEVADA.  $\times 10$ .

identical with the product of calcination in porcelain. This was called mullite after the Island of Mull.

#### DISTRIBUTION OF DEPOSITS

*Kyanite*.—Kyanite occurs in commercial quantities in the United States in North Carolina,<sup>47,30,22 48,12</sup> Virginia<sup>20,59,57</sup> and Georgia.<sup>39,1,44</sup> In addition to the large deposit now being worked near Burnsville, N. C., it is likely that other deposits capable of being worked exist in the mountainous region of the Black Mountain Range.<sup>13,30</sup> Noncommercial localities have been reported in Maryland,<sup>28</sup> Pennsylvania, Wyoming, Washington and California and in numerous places in the states already mentioned.<sup>20,21,39,48,58</sup> Kyanite is being mined in Imperial County, California, from a deposit covering about 15 acres at the base of the Chocolate Mountains, about three miles from Ogilby.\* Outside of

\* Letter by R. W. Ellison, Chief Chemist, Vitrefrax Corporation, Los Angeles, Cal.

the United States, kyanite occurs in many parts of the world in small amounts. The deposits of India are of chief importance commercially. Dunn<sup>10</sup> has estimated a minimum of 214,000 tons of kyanite at Lapsa Buru, India. Smaller and more or less inaccessible deposits exist at Ghagidih (20,000 tons), Badia-Bakra (10,000 tons) and Kanyluka (8,000 tons).

*Andalusite*.—The commercial exploitation of andalusite in the United States followed a lead suggested by Knopf,<sup>27</sup> who described andalusite from White Mountain, Mono County, Calif., in connection with studies conducted for the U. S. Geological Survey. Andalusite<sup>17,35</sup> is found in a number of separated occurrences on the northwestern slope of White Mountain. It is also being mined in the vicinity of Hawthorne, Mineral County, Nev. It occurs in small amounts in the Black Hills of South Dakota.<sup>8</sup> The mineral has also been found in sands in western Transvaal, Africa.<sup>34</sup> Spaenhauer has described an interesting occurrence of andalusite and kyanite in Switzerland<sup>46</sup> and Corin has discussed the origin of andalusite containing manganese in Belgium.

*Dumortierite*.—Dumortierite is found in commercial quantities near Oreana, Nev.<sup>19,37</sup> Numerous noncommercial occurrences have been mentioned in the literature.<sup>19,27</sup>

*Sillimanite*.—Although this mineral occurs in sillimanite schist in a number of places in the eastern United States, the impure character of the material and frequent association with quartz in the form of fine needles renders commercial development difficult. The large deposits at Khasi Hills, Assam and at Pipra, Rewa, India, are as yet too inaccessible by rail or highway to be of commercial value. Dunn<sup>10</sup> has estimated 100,000 tons of available sillimanite at Pipra, which is about 105 miles by trail from the nearest railroad. Sillimanite has also been described associated with corundum in the norite of the Bushveld igneous complex, west Lydenburg, Africa.<sup>15</sup>

#### POLITICAL AND COMMERCIAL CONTROL

Commercial deposits of the aluminum-silicate minerals are largely in the hands of private companies. The andalusite mine at White Mountain, Calif. and dumortierite mine at Oreana, Nev., are controlled by Champion Sillimanite Inc. Andalusite is also mined near Hawthorne, Mineral County, Nev., by the Tillotson Clay Products Co., Los Angeles, Calif. Kyanite is mined at Ogilby, Calif. by the Vitrefrax Corporation of Los Angeles. McLanahan-Watkins Co., of Charlotte Courthouse, Va., operate a kyanite deposit. Celo Mines Inc. controls several kyanite deposits in North Carolina, particularly the large operation at the north end of Black Mountain. Chas. F. Taylor and Sons, Cincinnati, Ohio, import kyanite from India, about 100 miles west of Calcutta.<sup>41</sup> In

view of the comparatively small cost of these minerals in the form of raw material in proportion to the manufacturing cost necessary to produce high-grade porcelain, refractory companies prefer to own and operate their own deposits. Such ownership enables them to stabilize plant production on a uniform method of treatment based on the raw material available.

### PRODUCTION AND CONSUMPTION

Because of the type of ownership, production figures are not regularly published. In the United States, production has been fairly steadily increasing since 1920. In the period 1922-1926, California produced 9394 tons<sup>38</sup> of aluminum silicate refractory minerals, largely andalusite. Production in recent years has probably been at about the same rate. During the past year and a half, dumortierite has been taken from stockpiles and mining has been discontinued. The McLanahan-Watkins Co. has been producing kyanite intermittently. The Vitrefrax Corporation estimates its production at about 800 tons of kyanite per year. Since the opening of the andalusite deposit at Hawthorne, Mineral County, Nev., on Sept., 1, 1935, five carloads have been shipped to the plant of the Tillotson Clay Products Co. in Los Angeles, for use in the manufacture of refractory products.\* Production of kyanite in India for 1933 was 4293 tons, by far the largest percentage being mined in the Singhbhum district.

Figures are not available for the amount of these materials used in the manufacture of the different porcelain bodies. The Champion Spark Plug Co., during a 10-year period, 1922-1932, using andalusite and dumortierite, produced 350,000,000 spark-plug cores.<sup>41</sup>

### PROSPECTING, EXPLORATION AND MINING

The occurrence of minerals of the andalusite group is largely limited to areas of metamorphic activity or to detrital or transported material derived from metamorphic rocks. Pegmatites and associated intrusives yield some andalusite and kyanite, but on the whole have not been commercially productive. Prospecting and exploration are largely confined to areas of surface exposure or near surface occurrence. Metamorphism is usually intense and results in rather a wide distribution of low-grade material. High-grade concentrations are comparatively rare.

Mining methods are for the most part extremely simple. Open cuts or short tunnels are used to penetrate the deposits. In the California and Nevada occurrences, the material is mined selectively and hand-sorted, the final selection of material being judged by frequent tests of specific gravity. In the piedmont belt the kyanite is mined in open

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\* Letter by Clifford Tillotson, Tillotson Clay Products Co., Los Angeles, Calif.

pits, and, wherever possible, in the residual deposits, separated from the enclosing material by washing. At Cleo Mines, Burnsville, N. C., a series of 20-ft. benches has been blasted parallel to the strike of the deposit, and, after secondary blasting, the ore is collected by drag scrapers on a loading platform.

#### PREPARATION FOR MARKET, TESTS AND SPECIFICATIONS

*Preparation.*—The andalusite of the Champion Sillimanite Co., in California, requires selective mining and hand-sorting before shipment to Detroit. At White Mountain, Calif., the andalusite must be carried by packmules down a steep trail,  $4\frac{1}{2}$  miles, and then transported by truck to a storage platform along the narrow-gauge railroad, 8 miles from the foot of the trail. At the siding in California and at the factory in Detroit, the material is spread horizontally in long, parallel strips, making a pile containing 2000 tons. For uniform grade the material is withdrawn at right angles to the original spreading direction. Dumortierite receives similar treatment.

At the plant the andalusite and dumortierite ore is crushed, passed over a magnetic separator, sized and distributed to storage bins. Bricks of dumortierite alone gradually swell and those of andalusite sag, a condition that can be remedied by a proportionate mixing of these components with each other or with other clay materials.<sup>38</sup> In making porcelain the components are mixed with water, reground to 320 mesh, the excess water removed in a filter press, the "cakes" stored for 10 days in an aging cellar to develop plasticity and then formed into "blocks" from which spark plugs may be made. Spark-plug cores are burned in a continuous kiln 300 ft. long at 3700° F., the process requiring four days for the cores to pass through the kiln.

The kyanite in the deposits of North Carolina, Georgia and Virginia is irregularly distributed, ranging from 2 to 80 per cent in volume in relation to the enclosing rock. The McLanahan-Watkins Co., at Charlotte Courthouse, Va., uses a simple wet gravity process for concentrating the ore, which occurs in a decomposed rock and residual clay 40 to 50 ft. deep. Cleo Mines Inc., Burnsville, N. C., uses a dry process; that is, the material is crushed and then fed to a machine with special hammers, which disintegrates without grinding the individual crystals. Screen concentration eliminates about one-third of the original ore with little loss of the kyanite, which is caught on the coarser mesh screens. An induction type magnetic separator removes, in addition to the abraded iron, the sulphides, garnet, biotite and a part of the muscovite, and a pneumatic concentrating table removes the quartz and small amount of feldspar and muscovite.\*

\* Paper by V. L. Mattson, presented before the American Ceramic Society, April 1, 1936.

The Vitrefrax Corporation, Ogilby, Calif., calcines the kyanite ore in a rotary kiln, which reduces the iron for removal by a magnetic separator and converts the alpha quartz to beta quartz. Quenching the calcine in water reconverts the beta quartz to alpha quartz, causing expansion. Later contraction produces a fine sand, which can be separated from the coarser kyanite calcine by slightly inclined shaking screens, the relatively pure kyanite fibers remaining on the screen.<sup>41</sup>

*Tests and Specifications.*—The minerals of the andalusite group are seldom found free from mineral associates. Some, such as muscovite, diaspore, pyrophyllite and sericite, do not detract from the value of the ore if present in moderate amounts. Quartz, however, which is one of the most persistent associates, must be kept as low as possible. Pyrite, magnetite and limonite, if present in more than traces, must be removed.

The most convenient commercial test is specific gravity. Commercial andalusite, for example, should have a specific gravity of at least 3.00 to be considered high grade. The Kraus Jolly balance or some other type of improved balance<sup>25</sup> for rapid weighing may be used.

#### MARKETING, USES AND PRICES

Synthetic mullite is important, for refractories for spark-plug porcelains, glass tanks in the glass-blowing industry, saggars, furnace-lining mufflers and parts of furnaces subjected to high temperatures.

The dumortierite from the mine at Oreana, Nev., is used exclusively for the manufacture of spark plugs by the Champion Spark Plug Co. The company markets both dumortierite and andalusite refractories as "Champion" sillimanite. The Vitrefrax Corporation produces refractory products under the trade names "Argon" and "Durex." The Corhart Refractories Co., in Louisville, Ky., manufactures a vitreous mullite refractory, using diaspore and kaolin, very suitable for glass-tank blocks. The kyanite and mullite produced by the Celo mines is being used for the manufacture of refractories, particularly for glasshouse refractories and refractory cements.\*

The cost of the raw material is the limiting factor in a more widespread use of the minerals of this group. When introduced, kyanite sold for \$100 a ton, but this was soon reduced to \$40 a ton and more recently the price has been slowly but steadily decreasing.<sup>61</sup> In the period 1922–1926, California produced 9394 tons, mostly andalusite, valued at \$301,790 or about \$32.13 per ton.<sup>38</sup> In 1932 kyanite was quoted in lump or concentrated form at from \$25 to \$80 per ton, according to purity, grain size and whether calcined or raw.<sup>59</sup> At the end of 1934 the Celo Mines Inc. quoted \$18 a short ton for 70 to 80 per cent kyanite, grading up to \$25 a ton for 90 per cent kyanite. An additional charge of \$15 a ton was made for calcining.<sup>61</sup>

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\* Letter by V. L. Mattson, Celo Mines Inc., Burnsville, N. C.

In 1928 the Singhbhum district in India produced 2241 tons of kyanite valued at £2509, a little over a pound per ton.<sup>38</sup> In 1933 the output was 4283 tons at £5220, a slight increase in price.<sup>61</sup> These prices are f.o.b. Amda, a station on the Bengal-Nagpur railroad. The price of sillimanite in England in 1929 was £11 per ton, but had been £14 per ton shortly before.<sup>10</sup>

High alumina-silica refractories were quoted in 1932 as follows: Corhart fused mullite, standard shapes \$200 per ton, P.B. sillimanite refractories (using kyanite from India, Chas. Taylor company) 9-in. brick \$500 a thousand, Babcock and Wilcox calcined kaolin fire brick \$260 a thousand, 9-in. diaspore brick (70 per cent alumina) \$145 a thousand.<sup>60</sup>

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## ASBESTOS

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**A**LTHOUGH asbestos deposits have been actively exploited for the past 70 years, it is only within the last 30 years that asbestos has become one of the important commodities of commerce, having required the needs of modern industry and science to develop its many uses. In early Greek literature, Pliny uses the word "asbestos" in reference to a fibrous mineral; Roman literature refers to "amiantus," which—as also the "asbestos" of the Greeks—was employed in the weaving of cremation cloth, and for lamp wicks. Because of its appearance, it was probably first considered an organic substance. Marco Polo, in writing of his travels in the thirteenth century through Siberia, in the district of Chinchutalus subject to the Great Kublai Khan, relates that: "A substance is likewise found of the nature of the salamander, for when woven into cloth, and thrown into the fire, it remains incombustible." He continues that this "fossil substance" was prepared, spun, and woven into cloth, and "in order to render the texture white, they put it in the fire and suffer it to remain there about an hour, when they draw it out uninjured by the flame and become as white as snow. And so again whenever they become dirty, they are bleached by being put into the fire."

Although the discovery of asbestos is attributed to the Romans, who mined it in a small way in the Alps, interest in it apparently lapsed and little mention is made of it in the literature of the Middle Ages. About 1710 to 1720, discoveries were made in the Ural Mountains, and 40 years later, during the reign of Peter I, a factory for the manufacture of asbestos articles was established in Russia. But the known uses were so few, and the demand so limited, that the industry subsequently disappeared. Later, interest in asbestos was revived in Europe, and technical investigation begun as to its properties and utility. From the year 1860, the search for deposits became widespread, and real interest in their development began to appear. The first modern attempt at exploitation was made by a London syndicate in the Aosta Valley of the Italian Alps, and production started in 1865. About the same time, asbestos was discovered between the villages of St. Joseph and St. Francis in Quebec. At

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the exhibition in London in 1862, a specimen of fine silky-fibered asbestos from the above locality was exhibited. No deposits were developed here however, and it was not until 1877 that the important discoveries at Thetford and Coleraine—in the same belt of serpentine rocks—were made. Production started the next year.

Prices at first were comparatively low, even for the best grades of fiber, but gradually increased after 1885. From that year the industry gathered impetus and expanded rapidly. At this time, systematic development began in Russia and, a few years later, in Africa. By 1905, while Canada was the chief source of supply, Russia and South Africa were producing, and Rhodesia was added to the list in 1908. For many years Canada led in production by a wide margin, but in 1934 was surpassed in gross value of asbestos produced by Russia.

### COMPOSITION AND PHYSICAL PROPERTIES

The word "asbestos" as used today is a term embracing the fibrous varieties of a number of minerals. Some of these, in their more common forms, are found as constituents of basic igneous rocks, and of major importance in the composition of certain metamorphic rocks. They are included in two mineralogical subdivisions: the amphibole group and one of the hydrous silicates of magnesium, serpentine. While these minerals are common, those possessing the necessary physical properties to be of commercial importance are not abundant; and, regardless of chemical composition, when crystallized with highly developed prismatic cleavage so that the mineral may be easily separated into fibers or filaments, it may be classified under the generalized commercial term,

There are sometimes considerable differences in the physical properties of different species of asbestos minerals, and often marked variations between specimens of the same mineral, even if obtained from near-by deposits or the same deposit. The mineral's value as asbestos is determined by certain characteristics that make it particularly fitted for some specific use or uses by industry. If it separates readily into long silky fibers of good tensile strength, it is generally suitable for spinning into yarn; if the fibers are less pliable but still strong, it will be more suited for use as a binder or reinforcing agent such as is necessary in the manufacture of asbestos-cement shingles or magnesia pipe covering. Short, easily separable fibers are used in the manufacture of asbestos paper, while coarser or more brittle types are unsuited for this purpose. Any of the several minerals used as asbestos are, to a degree, fireproof and acid-resistant, but some species may better withstand high temperatures or attack by acids than others; some are more hygroscopic than others—that is, have more tendency to absorb moisture from the atmosphere. So it may be realized there are several factors to be investigated in considering

the commercial value of any given kind or form of asbestos mineral. Such characteristics as hardness and specific gravity are relatively unimportant; but color and possible associated impurities do sometimes have a bearing on the value.

The cleavage of an asbestos mineral is responsible for the quality of fine silkiness of the fibers. Several of these minerals are characterized by an unusually high development of the prismatic cleavage, which permits separation along innumerable planes to a remarkable degree of fineness. Individual filaments have been measured to as small as  $1/25,000$  in. in diameter, and these, in turn, might be divided into still finer shreds.

The minerals that may occur in sufficiently fibrous form to be generally recognized as asbestos are: (1) amphiboles (sometimes called hornblende), under which are classified anthophyllite, tremolite, actinolite, crocidolite, amosite; (2) serpentine (or chrysotile).

### AMPHIBOLE

*Anthophyllite* is a silicate of, essentially, magnesium and iron, having the chemical formula  $(\text{MgFe})\text{SiO}_3$ , often with some replacement by aluminum and calcium. It occurs as mass fiber, the crystals being unoriented and interlacing; sometimes, in a radial arrangement. Commonly it is grayish white; occasionally, shades of green or blue. The fiber of this species is usually brittle, although sometimes it has considerable strength and toughness. It cannot, however, be considered of spinning quality, and its chief use is for insulation, in cement or plaster, or in the manufacture of paint. A certain short-fibered variety known as microasbestos—probably anthophyllite—is used with cement or asphalt in road building.

*Tremolite* is a calcium-magnesium silicate  $(\text{CaMg}_3(\text{SiO}_3)_4)$ . It occurs in masses of white to dark gray columnar or bladelike crystals, which generally are brittle, and are used principally for wall insulation or certain cemented products. This mineral has been found, however, occurring as fibers of sufficient length and flexibility to be of spinning grade. As it has particularly good acid-resisting quality, it is especially suited to the manufacture of filter pads, used in filtering fruit juices and acids.

*Actinolite* is similar in appearance to tremolite, but contains iron replacing some of the magnesium  $(\text{Ca}(\text{Mg.Fe})_3(\text{SiO}_3)_4)$ . It sometimes occurs as bright green or grayish green fibrous masses. The filaments are too brittle for spinning purposes, but are highly resistant to heat and acids; it is otherwise employed for the same uses as tremolite.

*Crocidolite*, because of its bluish gray or lavender-blue color, is commonly called "blue" asbestos. Occasionally it occurs in yellowish or rusty brown shades. This species is a complex, soda-iron silicate, the chemical formula of which is  $\text{NaFe}(\text{SiO}_3)_2 \cdot \text{FeSiO}_3$ . It is commercially the most important variety of amphibole asbestos, and occurs as cross-

fiber veins\* consisting of filaments of good length and flexibility, and can be spun into coarse yarn. It does not withstand high temperatures as well as the other asbestiform amphiboles, but is quite resistant to the action of chemicals. The purposes for which crocidolite is suitable are numerous and are included in many of the items under Uses.

*Amosite* may be described as an iron-rich amphibole, without the sodium molecule of crocidolite and, except for its higher iron content, similar in composition to anthophyllite. The percentage of water of crystallization is generally higher in crocidolite and amosite than in the other minerals of this group, analyses showing between 2.55 and 4.15 in the former, and 1.05 to 4.7 in the latter. It is commonly of an ash gray color, or more rarely white or pale brown, and occurs in cross-fiber veins several inches thick, thereby having exceptional fiber length. The fibers are pliable but of rather coarse texture, and it is not used extensively in spinning. It has been found satisfactory as a binder, or reinforcing, for heat-insulating blocks such as magnesia pipe covering.

### SERPENTINE

Serpentine is a hydrous silicate of magnesium having the chemical formula  $H_4Mg_3Si_2O_{10}$ . It is—as, in fact, are the asbestiform varieties of amphibole—a secondary mineral, being formed by the alteration of other minerals. It occurs in several forms: the dense, massive variety is common serpentine; that composed of bladed, columnar, or coarsely fibrous crystals is called picrolite; while the highly fibrous variety is known as chrysotile.

*Chrysotile*.—Of all the minerals used industrially as asbestos, chrysotile constitutes by far the largest percentage of the world's supply. Veins of cross-fiber chrysotile are usually of various shades of green, although sometimes light yellow or cream color and, in some deposits, of a light brownish shade. When the crystals are pulled apart, or “opened,” the color of the fibrous mass is usually white—as is true of most kinds of asbestos, except crocidolite, which retains its bluish hue. The better grades of chrysotile are characterized by their extreme fineness of fiber, or “silkeness,” which, coupled with high tensile strength and sufficient length, make it particularly valued for spinning. The percentage of water of crystallization, which may have some bearing on the fiber flexibility of all varieties, is highest in chrysotile, being commonly from 10 to 13 per cent. This factor of constitution affects the heat-resisting qualities adversely, chrysotile being weakened at lower temperatures than amphibole asbestos, with the exception of crocidolite.

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\* By common usage, the word “veins” is accepted, although pertaining here to tabular bodies of dimensions which, in the more widely used sense, would be called veinlets or stringers.

Magnetite is a mineral that is sometimes closely associated with the structure of a chrysotile vein. When it is present the fiber is less suited for electrical insulation. Some deposits are iron-free, and the fiber from these is particularly prized for electrical purposes. Generally speaking, throughout the wide range of uses for which asbestos is adapted—from short grades of dustlike consistency, to the longest grades—chrysotile supplies the major portion for nearly all of the major uses.

### ORIGIN AND MODE OF OCCURRENCE

An asbestos deposit seldom contains more than one asbestos mineral. Two or more physical forms of the same mineral may occur closely associated, and one variety may be found in rocks of widely divergent origin and character. The main feature in common to all deposits is some degree of metamorphism, this action, in many cases having been severe. Dependent upon the type of metamorphism and the kind of rock affected, a generalized classification may be arranged:

1. Serpentine type (developing chrysotile asbestos). Alteration to serpentine of:
  - a. Basic igneous rocks such as dunite and peridotite.
  - b. Sedimentary rocks such as dolomite and limestone.
2. Amphibole type. Amphibole asbestos developed in:
  - a. Impure shales and slaty quartzites such as the siliceous ferruginous slates of the so-called banded iron-stone formation.
  - b. Basic igneous rocks.
  - c. Highly altered rocks of gneissoid or schistose character, of igneous or sedimentary origin; gneiss, gneissoid schist, or crystalline schist of high magnesia content.

Asbestos is commonly found in three forms, according to the mode of occurrence:

*Cross-fiber*, when the fibers are arranged normal to the vein walls; the fiber length is thereby limited to the vein width and is often less, due to a break, or parting, in the vein;

*Slip-fiber*, when the fibers lie in the same plane as the vein or slippage plane upon which it is formed;

*Mass-fiber*, when formed as an aggregate of interlaced unoriented fibers, or as stellate groups of radiating needles.

Some 90 per cent of the world's asbestos supply is derived from deposits of serpentine asbestos in dunite and peridotite. These are intrusive rocks composed essentially of olivine, peridotite differing from dunite in that it contains an appreciable percentage of pyroxene. Large masses of these rocks have undergone various degrees of serpentinization. This alteration was probably accomplished by solutions emanating from the same magmatic source as the basic intrusives themselves or, more directly, from solutions accompanying later acidic intrusions such as granite or aplite. By these the magnesian silicate, olivine, was altered

to the hydrous magnesian silicate, serpentine. In places, the entire mass was permeated sufficiently to produce a widespread and high degree of serpentinization. Chrysotile veinlets were formed along fractures, where conditions were favorable.

Certain portions of the formation, commonly forming roughly ellipsoidal bodies, and probably resulting from segregation during solidification of the original rock, were especially favorable to vein development. In these bodies, which are often fairly extensive, a network of veins may be found constituting up to 15 or 20 per cent of the volume. These chrysotile veins range from a fraction of an inch to one, two, or more inches wide, and are generally short, or continuous for no more than 50 to 100 ft. They may intersect each other at various angles or may lie in closely spaced parallel planes, giving the appearance of stratification. This latter arrangement is called "ribbon structure."

Aside from these higher grade bodies, the serpentine rock often contains also a low percentage of cross-fiber, and, in some cases, up to 5 or 10 per cent or more of slip-fiber. Slip-fiber is more abundant in the softer, more highly serpentinized zones, although frequently it occurs on faulted or slickensided surfaces in the more massive rock. Apparently it was formed with the aid of dynamic action; by the movement producing a fault, or the slight displacement on a slippage plane; or, in a mass which has yielded to pressure by "flowing" in the solid state, to the extent of developing a scalelike structure. In the latter case, slip-fiber is found in the slickensided serpentine covering the surface of each small scale.

Examples of the foregoing types of chrysotile deposits are numerous in the serpentine belt that extends from northern Vermont northeasterly through the Eastern Townships of Quebec. The bulk of production is from deposits worked primarily for the cross-fiber content, although slip-fiber occurs to some extent in most of the ore bodies. A few mines are operated on ore which contains little or no cross-fiber.

The asbestos deposits being mined in the Shabani district of Southern Rhodesia, and those of the Bajenova district in the Urals, Russia, are similar in mode of occurrence to the cross-fiber bodies of Quebec. In Cyprus, small veins of chrysotile are found in the periphery of a large peridotite plug.

Chrysotile veins occur in limestone and dolomite within bands and lenses of serpentine, or in the outside shell surrounding nodules or larger ellipsoidal bodies of massive serpentine; they form as successive layers of asbestos and serpentine enveloping the serpentine core. The more extensive deposits of this type are those in bands or flat-lying lenses of serpentine; the veins occurring as layers paralleling the bedding of the limestone. In Arizona, deposits are found in the portions of a dolomitic limestone associated with diabase sills. Solutions from the diabase have serpentinized these parts of the limestone, with the accompanying



development of asbestos veins. Similar occurrences have been worked in the Carolina district of the Transvaal and in Minusinsk, Siberia.

Of the amphibole varieties, crocidolite and amosite are the only ones commonly having the cross-fiber habit. Both minerals occur as interbedded veins in banded ironstone, which is a silicified slate formation containing iron. Commercially important deposits of crocidolite are found in Cape of Good Hope, South Africa. Here the ironstone formation is extensive and occurrences are widely distributed throughout the belt. The fiber ranges from less than  $\frac{1}{2}$  in. to 2 in. and longer. The proportion of long fiber to short is greater than in deposits of chrysotile, such as those of Canada, Russia and Rhodesia, although the chrysotile mined in the Barberton district of the Transvaal is said to be even longer than the crocidolite from its neighboring state, Cape of Good Hope.

Amosite is mined in northeastern Transvaal, where it also occurs in banded ironstone formation. There are no intrusive rocks associated with the deposits in this formation.<sup>26</sup> Its occurrence is very similar to that of crocidolite, and the two minerals are closely related. Crocidolite is found in the western part of the amosite belt, both varieties being recovered from some of the workings. Amosite fiber is unusually long, averaging about 6 in., and ranging upwards to 10 or 12 inches.

The other varieties of asbestiform amphibole, anthophyllite, actinolite and tremolite, occur largely as mass-fiber or, in some cases, as slip-fiber. In deposits such as those of Sall Mountain, Georgia, anthophyllite occupies pockets and lenses in a gneissic rock of probably igneous origin. The ore bodies occur as fibrous masses, which may contain up to 90 or 95 per cent commercial fiber. Near the surface, where subjected to weathering, the fiber is softer and more suitable for use than below the weathered zone.<sup>2</sup> Anthophyllite is also found as slip-fiber occupying shear zones, and rarely as cross-fiber. It is generally harsh and rather brittle, but there is a hard, dense type, which may be broken down into a soft, fluffy mass. It is rarely found of sufficient length and silkiness to be of spinning quality.

In Italy the early production consisted of tremolite. The fibers are often long but frequently too coarse to be valued for spinning.

#### DISTRIBUTION OF DEPOSITS

The known asbestos resources of the United States are of limited extent. Exploitation and development have been retarded by mining and transportation difficulties in some localities, but there is nowhere indication of extensive deposits such as are found in several other countries.

The serpentine belt that extends from Quebec into northern Vermont, has, in Vermont, yielded comparatively small tonnages of the medium

<sup>27</sup> References are at the end of the paper.

and short grades of chrysotile asbestos. The fiber is of good quality, but no extensive deposits have been developed. The limestone deposits of Gila County, Arizona, have been worked, producing a very good grade of chrysotile. However, mining and transportation costs have discouraged development; mills have been built, but the mines are active only when high prices prevail. Other occurrences of chrysotile have been explored and, in some cases, small amounts produced in California, Montana, Wyoming, North Carolina and Virginia.

The largest tonnages of amphibole asbestos produced in the United States have come from the Sall Mountain district of Georgia. Here, owing to the fact that the best material is within the zone of weathering, the deposits are shallow, and reserves apparently have neared

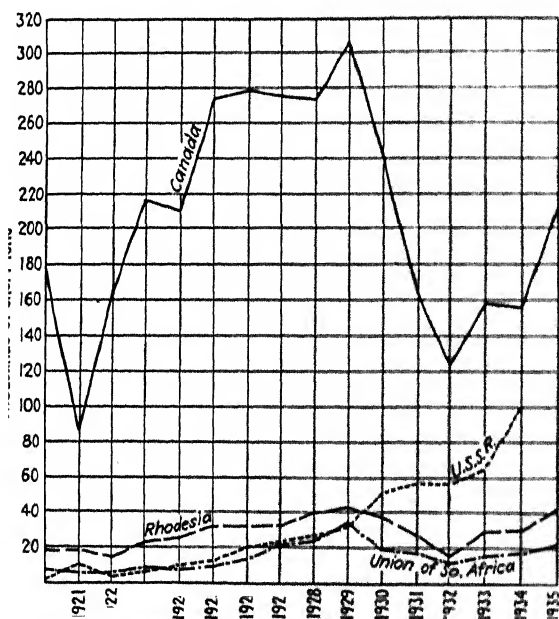


FIG. 1.—ASBESTOS PRODUCTION BY COUNTRIES.

depletion. Small-scale operations, working the shear zones in a gneissoid schist near Pylesville, Md., yield anthophyllite suitable for acid filter. Some development work has been done on amphibole occurrences in Montana, North Carolina, Virginia, Idaho, California, Oregon and Washington, but no potentially large supplies have been found.

Outside of the United States a number of extensive asbestos deposits have been proved. Chrysotile occurrences of the type found in Quebec, Southern Rhodesia and the Bajenova district of Russia probably extend to considerable depth, which would add to the large reserves already developed. Those of the Barberton district, in the Transvaal, containing chrysotile have not been intensively exploited though from 8,000 to 17,000

tons per year has been produced. Difficult transportation, and the fact that the beds are banded and dip into the ground make extensive underground development necessary to block out large tonnages. Some of the chrysotile deposits of the Carolina district, of the same province, occur in serpentinized basic igneous rock, and are of the same type of occurrence as those mentioned above, while others are in dolomite and similar to those of Arizona, and of Minusinsk, Siberia. No large reserves have been disclosed. Cyprus has a supply of short-fibered chrysotile.

The only commercially important occurrences of crocidolite and amosite are those of South Africa, where the fiber-bearing belts of Cape of Good Hope and the Transvaal cover a large area and have been worked

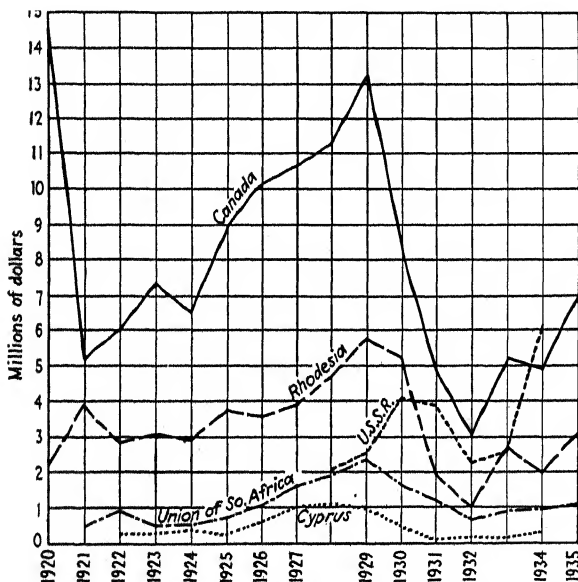


FIG. 2.—VALUE OF ASBESTOS PRODUCTION.

as small operations in many places throughout the extensive ironstone formation. Many other countries have known deposits, most commonly of chrysotile asbestos, which are small, low grade, or developed to only a limited extent. Among these are Italy, Finland, Czechoslovakia, India, China, Western Australia, New South Wales, New Zealand, Madagascar, Turkey and Venezuela.

#### POLITICAL AND COMMERCIAL CONTROL

Aside from those of Russia, all of the large producing deposits of asbestos lie within the British Empire. English capital controls the mines of Rhodesia, South Africa, and Canada, although in Canada it shares this with large interests of the United States and Canada. English

own the productive area of Cyprus. The Russian mines and resources are, of course, exclusively owned by the State.

The United States is by far the greatest consumer of asbestos, and imports the larger part of its requirements from Canada, buying some 90 per cent by quantity, or 80 per cent by value, from this source. This normally accounts for over 30 per cent of the Canadian production. For many years, England, France, Germany and Belgium imported the major portion of their supply from Canada, but the African mines now furnish much of England's large manufacturing needs, while Germany, Belgium, Italy and central European states are supplied, in varying proportions, from Canada, Russia, and, to a lesser extent, from Rhodesia, while France, Spain and Portugal draw supplies from Canada and Rhodesia.

The rapidly expanding production of asbestos in Russia has disturbed world markets but to a much smaller degree than might have been anticipated. Russia's program calls for increased manufacture and home consumption of asbestos products, with the result that much of the raw product is not produced for export, and therefore is not competitive with that from other countries. It now ranks second only to the United States in the quantity of asbestos used.

Japan produces a negligible percentage of the fiber it uses. It imports largely from Canada, and a little from Russia and Africa.

For the shorter, lower priced grades, Canada holds an advantageous position. Much of this material is used in the United States, and because freight charges constitute a larger proportion of the delivered cost than for the higher priced fibers, its proximity to these markets makes it difficult for other countries to compete in these grades.

Asbestos is an important commodity of international trade. Aside from Russia, none of the important producing countries are substantial consumers of their raw product, nor are any of the large consuming countries—other than Russia—able to supply more than a small part of their own needs.

### PROSPECTING AND MINING

Asbestos deposits are resistant to weathering, and often are less affected by erosion than the surrounding rocks. For this reason outcrops frequently occupy knolls or ridges, and are more easily seen than deposits of less stable minerals. The kind of formation in which the more common types of deposits occur is easily recognized, and prospecting may be thus confined within definite boundaries. When an outcrop is found, or uncovered by trenching or stripping, the grade of ore exposed can be closely estimated by visual inspection, particularly when it has been broken into by drilling and blasting. Asbestos veins, where long exposed to weathering, are often discolored as a result of the oxidation of impurities. The fibers generally remain in place between the vein walls, except for the upper few inches that have been exposed.

Where overburden is present, the usual methods of trenching and stripping are used to reach the solid rock. Further exploration may be carried on by diamond or calyx drilling; the calyx, or shot drill, has the advantage of giving a larger core and, therefore, a better sample for examination, but is not practical for deep drilling. The majority of deposits, however, are developed by test pits, which are simply continued and enlarged into quarries when results are satisfactory.

Exploration by tunneling or other methods of underground excavation, or by diamond-drilling from these workings, is sometimes advisable, depending upon the position of the area to be explored.

The percentage of asbestos content, when derived by other means than visual examination and estimate, is determined by mill recovery from large bulk samples, or by laboratory methods simulating the operation of milling.

Many of the standard open-cast and underground mining methods are used in the extraction of asbestos ore. A few innovations, particularly in handling the rock of open-cast workings, are peculiar to the industry. Underground mining systems are similar to some of those used in metal mining, with occasional variations to suit special conditions.

Open-pit workings have a wide range of size and shape, depending upon the area and depth of the deposit, and the extent to which it has been exploited. In these the rock is broken in such a manner as to allow it to fall to the quarry bottom or the faces are advanced in a series of benches. The ore in the majority of deposits may be classed as soft or medium hard, to drill and break. Air drills of the common hammer type are in general use, mounted on tripods for drilling flat breast holes, and often for steep bench holes as well.

Holes with this equipment range up to 18 ft. in depth. Deeper drilling, to 40 ft. or more, is accomplished by using a heavy drill with an A-frame and slide arrangement; or drill carriages are used, either type of equipment allowing steel changes at intervals up to 10 ft. For block-holing and other short holes, various sizes of jackhammers are used, in accordance with standard practice. Wet drilling is uncommon, as water mixed with asbestos fiber forms a spongy mass, which is difficult to clear from the holes. The dust, at least from most Canadian asbestos ores, has no evident deleterious effect on the workmen's health.

The broken rock is handled in various ways. Hand-loading methods are common even in some of the larger operations in Canada, and are used almost entirely in Russia and Africa. These methods persist partly because they permit more thorough sorting of waste rock. Ore is shoveled or barred-down into open-mouthed steel boxes, or shoveled directly into cars or other vehicles. Where boxes are used, they are handled and dumped into cars by means of boom derricks, steam cranes or overhead cableways. If cableways are used the boxes are hoisted directly to sur-

face, obviating other hoisting facilities. Elaborate systems of overhead cableways were developed in the Thetford mines district of Quebec, but are little used now.

Some pits are relatively shallow to the area covered, and ore trains are run directly to the working faces. One large mine uses a spiral track layout following benches from which the mining is carried on. Standard-gauge steam or electric locomotives, and ore cars are run to the pit bottom over several miles of track. In other mines, where the relative depth precludes the use of locomotives to reach the pit bottom, hoisting is used: on an incline, through incline tunnel, or by shaft. In any case, where large-capacity ore cars are brought to the working faces, the usual method of loading is by power shovel, or by cranes handling steel boxes. The boxes are loaded by hand, the reason being that more effective separation of waste rock from ore can be achieved in the quarry by hand-loading.

Extraction by the glory-hole system is used by some mines, and may be effected from any type of underground opening. Raises are put up from an established level to surface, where the ore is broken down by funneling out the top of the raises, and is drawn off through these into cars.

Various types of underground mining methods have been used in asbestos mines. For flat-lying deposits, under barren formation, like- ing many of those in sedimentary rocks, flat stope or a system of room-and-pillar mining is necessary. For steeper or deep deposits, shrinkage stoping, and, at least once, sublevel stoping has been used. In the most compact serpentine rock, stope widths can be safely carried at 40 ft. or more. A recent development in one mine of the Thetford district is the application of a form of block caving. In this mine the method is briefly as follows: Opening is by vertical shaft, and one main haulage level is established at a depth of 500 ft. from surface. The latter is served by electric locomotive and 5-ton cars. The overlying ore is divided into blocks 160 ft. square in plan. A block is developed by four grizzly drifts running through it at 40-ft. intervals, and at an elevation of 45 ft. above the haulage level. These drifts are timbered with 6-in. H-beams, and finished flush with concrete. (Steel timbering is used throughout the mine in preference to wood, as it is desirable to prevent wood chips from contaminating the fiber.) Each pair of grizzly drifts is served by one drift on the haulage level below, with which it is connected by ore-pass raises. Grizzlies of heavy steel rails with 16-in. opening between rails are constructed at the top of each raise. From each grizzly—these being spaced at 20-ft. intervals along the drifts—two finger raises are put up, one on each side of the drift. At 20 ft. higher, the block is completely undercut by driving drifts and blasting out the intervening pillars. The finger raises are funneled out to permit large pieces of ore to be reached and broken up at the grizzlies, when actual extraction is begun. In order to weaken the boundaries of the block, raises are put up at each corner and

connected by drifts. These are called boundary cutoff drifts, and are spaced according to the character of the rock. It is desirable that the material cave within vertical walls, and these boundary drifts form a line of weakness for controlling the break. All development work having been completed and the pillars of the undercut level shot out, the ore breaks down from its own weight. As the broken ore supporting the back is drawn off through the finger raises, by working it through the grizzlies, more caves to take its place. This action continues through to surface. Where it is necessary to protect property in the vicinity of the mine workings, the walls of the caved block are retained by backfilling with mill tailings (these are of the consistency of fine gravel), which are dumped in from surface, and follow the broken ore as a plug as it is drawn off.

### PREPARATION FOR MARKET

In the early days of production, asbestos was supplied to the market entirely in the crude form, and the only portion of the asbestos content of an ore body that was recovered consisted of the larger veins, which could be conveniently picked up as lumps and roughly dressed by hand methods. In 1888, a few years after production had started in the Quebec fields, mechanical means began to be developed to aid in preparing cleaner, more uniform crude, and to recover some of the shorter fiber then being rejected. Difficulties were encountered, but by 1896 sufficient progress had been made with milling to produce important tonnages of fiberized asbestos. The demand for these fibers increased, and milling practice has improved and expanded, until at present there are many mills of daily capacities from 1000 to 2000 tons, and individual plants capable of treating 4000 to 6000 tons of ore daily. Nevertheless, hand dressing persists in the recovery and preliminary preparation of crudes. It is an effective means of recovering the long fiber without subjecting it to the rougher treatment of machines, with the accompanying effect of sacrificing fiber length. A much larger proportion of the asbestos is recovered by hand in some fields than in others.

The Canadian mines are highly mechanized, and Russia, in recent years, has followed the methods developed here. The Rhodesian asbestos mines employ a larger percentage of hand labor for fiber recovery, but milling has become an important part of the process. Hand methods predominate in the South African fields, but even there, mills with elaborate flowsheets have been built. The one mill in operation in Vermont closely follows Quebec practice; those of Georgia and Arizona are small. The following brief description of Canadian practice includes the essentials of most of the methods used elsewhere.

*Cobbing.*—When the ore is broken in mining, many of the larger veins are partly loosened from their walls. Where accessible, these pieces

of vein material are picked up by hand immediately. Some lumps retain portions of the wall rock, which are freed by the blow of a hammer. Further recovery of the larger pieces of cross-fiber veins (slip-fiber is not generally of sufficient value to be handled in this way) is effected sometimes on picking belts or tables before or after the primary crusher. The material thus obtained is further treated in a department separate from milling; and the whole operation is known as cobbing. The rough crude is dried and screened, after which each piece that has any adhering rock or contains impurities (massive serpentine and magnetic iron are the more common impurities) is pounded by hand with a special hammer, to break up and free the undesirable portion. Lumps that are off-color, or otherwise below standard in quality, are rejected. The best material, of a fiber length of  $\frac{3}{4}$  to 1 in. and above, is classified as No. 1 Crude; the remainder, down to  $\frac{1}{2}$  or  $\frac{3}{8}$  in., is graded as No. 2 Crude. After cobbing, each grade is further cleaned on screens. Except where special preparation is desired, the crude is now ready for bagging and shipment. In some places, run-of-mine crude or other classes are produced. The cobbing and screening rejects are sent to the mill, or treated separately as special grades.

*Milling.*—The release of asbestos from the rock and from accompanying impurities is effected in milling by following much the same principle as in cobbing. The fibrous structure is strong and tough, while the gangue is brittle. Crushing, impact, and grinding break up the rock and associated minerals; while the asbestos is simply separated along its cleavage planes and converted into a mass of fibers in a fluffed condition. A certain amount of fiber is cut or broken but, to minimize this, the machines used are carefully selected or specially designed. Separation of the released material cannot depend on differences of gangue and the mineral to be won, such as chemical composition or specific gravity, as is the basis of treatment of most ores. The principle by which asbestos is removed from the crushed ore is that the volume of the mineral is increased by any action that tends to separate the individual crystals, thus converting it into a fluffed condition. Because of this, the ore is adaptable to screening to remove the fines produced in crushing, and the fiber to being removed by a current of liquid or air. All existing mills use air as the medium of separation, and the ore must be dry for effective milling.

The earlier mills effected separation by blowing the crushed or ground ore into long chambers; the heavier rock particles falling first and the more highly fluffed fiber being carried to the farther end. Later practice developed the use of suction hoods, placed at the end of shaking screens, operating on the principle of a vacuum cleaner. Large fans produce the necessary vacuum, and hoods, with a narrow opening extending across the lower end of a screen, distribute the air currents, allowing the fiber to



be swept from the rock and aspirated through large sheet-iron pipes. Enlarged sections of the circuit, in the form of collectors, recover the fiber. Modern mills, in order to recover the dust and very light, short fiber not caught by the collectors, discharge the air from the fans into large dust sheds, where this fine material may settle.

There is considerable variation in the equipment of one mill as compared to another, but the flowsheet of each aims to have machinery that most effectively frees and separates the asbestos from the ore with the least injury to the fibers, and adequate to recover all of the salable fiber and by-product grades. Some ore bodies contain principally short fiber, and others a large percentage of long; either characteristic making for simplified milling, particularly the latter when remoteness from the market makes it uneconomical to ship the cheaper grades. Canadian mines, because many of the ore bodies contain appreciable amounts of both long and short fiber, and because the relative proximity to markets makes the production of low-priced grades possible, have developed milling practice to a high degree, and produce by far the greatest range of fiber grades. As a rough guide to the process and the kind of equipment used, a generalized flowsheet, showing alternate machines of different mills, is given herewith.

### *Generalized Flowsheet*

#### PRIMARY CRUSHING

Jaw or gyratory crusher

Picking belt or tables (recovery of crude and, in some cases, rejection of waste)

Grizzly

Jaw crusher, gyratory, or rolls

Grizzly

Gyratory or swing-hammer crusher

} or cone crusher

#### DRYING (Material size about 2 inches)

Cylindrical rotary drier or vertical stack drier

#### BINS

Storage to provide uniform mill feed, curing, and surge

Capacities range up to 25,000 tons

#### MILL (Secondary crushing and primary separation)

Screens and suctions

Cone crusher, hammer mill, gyratory or rolls

Screens and suctions

Torrey cyclone, hammer mill, cone crusher, rolls, or jumbos

Screens and suctions

Jumbos, cyclone, or ball mill (seldom)

Screens and suctions

Sometimes—one or more repetitions of the last stage, generally using jumbos. This may be in the form of a separate tailing unit

Tailings conveyed to dump

The fiber from the preliminary separation contains sand and scales of rock, etc. This must be eliminated by further screening, and lifting the fiber by suction. The asbestos recovered at the head of the mill is the

longest, and is generally finished separately. It is graded on flat screens or, more commonly, in stationary tromeels called graders, which take out the correct amount of the shorter portion to arrive at the desired grade, besides aiding materially in the cleaning process. The shorter fiber is further cleaned on screens, and, with similar fiber recovered in the primary separation, is sent to other graders to produce the second longest grade. In some mills, the operation is repeated to make three, four, or more grades. Additional screening and, sometimes, grading stages are used after the preliminary grading in order to produce cleaner fiber, and arrive at the correct test. At this point graders may prepare the fiber in a more opened, or fluffed, condition, if desired.

The material collected in the dust shed is returned to the mill, where short fiber is extracted, and the dust used in producing various extremely short grades called "floats."

The finished fibers fall into bins from which they are bagged (100 or 125 lb.) by hand, or with the aid of bagging machines.

While a limited number of fiber grades can be made in a mill at one time, by equipment adjustment and minor alterations other combinations of grades can be readily produced. An explanation of grading and testing will be given on another page.

### MACHINERY

Certain of the equipment peculiar to asbestos milling requires a brief description:

*Hammer Mill.*—The hammer mill consists of a modified cylindrical housing, one size commonly used being 54 in. long and about 22 in. at the shortest radius (inside dimensions). It is lined with manganese-steel plates. A horizontal central shaft is fitted with disks and spacers, and, near the periphery of these disks, six equally spaced smaller shafts are passed. On these shafts are hung steel arms or "hammers" at  $2\frac{1}{2}$ -in. intervals throughout their length. The assembly is rotated at high speed, causing the hammers to swing outward. The rock, which is fed from the top of the housing, is struck by the revolving hammers and thrown against the steel lining, being crushed by impact. It is discharged through an opening that runs the length of the bottom of the housing. The opening is either wide enough to allow free discharge or is constricted by grids or bars.

A similar machine has been fitted with air suction, and used as the principal equipment in the recovery of anthophyllite asbestos in Georgia.<sup>2</sup>

*Cyclones.*—Two principal types of cyclones are used. The Torrey cyclone consists of a vertical, cylindrical shell enclosing a central upright shaft. Ore, fed at the top, falls onto a small table revolving rapidly with the shaft. Centrifugal force throws the material to the outside of the table, from which it is guided by vanes and caused to impinge on deeply

grooved castings lining this part of the shell. Falling from there into a conical hopper, the rock is guided to a second table, from which it is again thrown and further crushed by impact.

The other cyclone is a smaller machine. Two, heavy, three-bladed propeller-like beaters are arranged close together on separate horizontal shafts. In the Laurie machine these are revolved in opposite directions, while in another make, the Pharo cyclone, they rotate in the same direction. Feed comes in at one end; falling between the beaters (which are face to face), it is broken by impact on the blades and against the sides of the bowl-shaped receptacle, and ground under the beaters. Discharge is upward, and is induced by the material being thrown and blown out by the high speed of revolution.

*The Jumbo.*—This machine has largely replaced the Laurie and Pharo cyclones. It consists of a horizontal cylinder, 6 or 8 ft. long, assembled with cast-iron ends and corrugated cast-iron liners. A number of arms, fitted with heavy, detachable tips, are clamped on a horizontal shaft, and revolve at a moderate rate. The feed, entering the top at one end, is subjected to a rubbing and grinding action as it is moved the length of the machine by the beater tips, which have beveled faces of a pitch sufficient to impart forward motion to the feed at the desired rate. Discharge is through a hole in the bottom at the end opposite the feed.

*Driers.*—Rotary driers are 40 to 60 ft. long and 4 to 6 ft. in diameter, and inclined at a flat angle. Hot air from a firebox passes from one end to the other of this cylinder, and is brought more closely in contact with the material being dried, by large angle irons running lengthwise on the inside of the shell, which cause the rock to be lifted and cascaded as the machine slowly revolves.

The vertical type of drier is built as a square stack 50 ft. high and 7 by 7 ft. in cross section. The crushed rock falls through a rising current of hot air and gases coming directly from a firebox built on one side at the bottom. The falling material is retarded by grid bars placed at regular intervals throughout the height of the stack.

*Screens.*—Various sizes and types of screens are employed. Shaking screens actuated by eccentrics are the most common. The speed, length of stroke and slope used vary widely. Usual sizes are from 3 to 5 ft. wide and from 8 to 12 ft. or more long. Perforated steel plate is more generally employed than wire mesh, particularly on rock screens. Perforated plate with holes up to  $\frac{3}{8}$  in., and larger for scalping screens, is used at the head end of the mill. Smaller openings down to  $\frac{1}{32}$  in. are required for very fine material. Different sizes of wire screening, ranging in mesh from 3 to 24 to the inch, are frequently used on fiber-cleaning screens. Vibrating screens find limited application in some mills.

*Suctions.*—The hood through which fiber is lifted from the lower end of a screen is adjustable, and has approximately the same cross-sectional

area at the mouth as the pipe into which it converges. The width of opening is generally from 2 to 5 in., and piping leading to the collector is from 12 to 20 in. in diameter. One fan generally furnishes two or more suctions, which may lead into one collector. For a suction pipe 15 in. in diameter, from 10 to 15 hp. at the fan is required to produce the desired flow of air and lifting power.

*Graders.*—A grader is a cylinder of perforated steel plate through which passes a central shaft. Arms are clamped to the shaft, and detachable tips bolted to the end of the arms. A popular size is 8 ft. long and 28 in. in diameter. The arms and tips are twisted at a slight angle, which, with the speed of revolution of the shaft, governs the rate at which the fiber is moved through the machine. The speed is usually between 400 and 900 r.p.m. Material enters one end; undersize is forced through the perforations of the plate by the tips (there is a small clearance between tips and shell), and oversize is discharged at the opposite end.

### TESTS AND SPECIFICATIONS

The grades in which fiber is classified are controlled within stated limits by means of a standard testing machine developed in the Quebec field, and almost universally accepted as the unit of measure by which milled asbestos is sold. This machine consists of a nest of four rectangular screens held in wooden frames, placed on a table that is actuated by a shaft and eccentric. The bottom box serves as a pan, and the screen of each of the three superimposed boxes is of successively larger mesh. The machine, boxes and size of wire and mesh are made to exact specifications. The screen of the top box has  $\frac{1}{2}$ -in. openings between wires, that of the second is 4 mesh, and of the third, 10 mesh. Sixteen ounces of the fiber to be tested is placed on the upper screen, and a cover clamped over the top, securely holding the nest of boxes. The machine is started, runs at 300 r.p.m. for two minutes, and stops automatically. The boxes are removed; the fiber remaining in each is weighed and recorded to the nearest tenth of an ounce. With this machine, fiber can be tested ranging from nearly all minus 10 mesh to that of sufficient length to be largely retained on the top screen. Ro-Tap machines, using a nest of small sieves, are also employed, assisting in the control of production of short fibers.

Until recent years, each company designated its own grades. This caused confusion and inconvenience to the buyer. In Canada, the condition has been remedied by the Quebec Asbestos Producers' Association, which, in conjunction with the Government, has agreed upon uniform design of testing equipment, a standard control in the form of a Government testing machine, and standard markings for the various grades. Fibers are divided into groups, and each group subdivided into grades, which are designated by letter prefixed by the group number.

- Group No. 1. Crude No. 1 ( $\frac{3}{4}$ -in. staple and longer).
- Group No. 2. Crude No. 2 ( $\frac{3}{8}$ -in. staple up to  $\frac{3}{4}$ -in.). Crude run of mine (unsorted crudes). Crudes, sundry (crudes other than above specified).
- Group No. 3. Textile and spinning fibers (testing 0-8-6-2 and over).
- Group No. 4. Shingle fibers (testing below 0-8-6-2 and including 0-1.5-9.5-5.0).
- Group No. 5. Paper fibers (testing below 0-1.5-9.5-5.0 and including 0-0-8-8).
- Group No. 6. Waste, stucco, or plaster fibers (testing below 0-0-8-8 and over 0-0-5-11).
- Group No. 7. Refuse or shorts (testing 0-0-5-11 and below).
- Group No. 8. Sand.
- Group No. 9. Gravel and stone.

As examples of the manner in which these groups are subdivided into grades; a 3K fiber is one of the spinning and textile group, having a minimum test of 4-7-4-1; a 5R fiber is one of the paper-fiber group, and has a minimum test of 0-0-10-6.

Some plants produce two or more types of the same grade, characterized chiefly by the degree to which the fiber is fluffed, or opened.

#### MARKETING, USES AND PRICE

Most of the raw asbestos produced is sold to manufacturers of asbestos products. Agencies and representative firms handle part of the business, and in some cases act as jobbers, but most of the fiber is shipped direct from mine to consumer. Samples are usually submitted to the customer, and sales made on guaranteed test and quality. Formerly, large and long-term contracts were common, but now contracts are made to terminate at the end of the current year. The supplies of raw asbestos are in strong hands, as well as much of the manufacturing, and close cooperation between the two is usually found. Mutual understanding is particularly desirable in the asbestos industry, since, to supply the manufacturer's needs to the best advantage—particularly in the milled fiber field—the producer should be familiar with conditions in order to prepare the material to suit the particular use and process for which it is required. Several of the large manufacturing companies control their own asbestos mines.

More of the fiber, in recent years, is sold in a condition ready for use in the plant without the necessity of further opening and cleaning action. Some mill fibers and all crudes, however, are supplied in a less opened state, and the manufacturer subjects it to the final stages of fluffing and elimination of waste.

The uses for asbestos are many and diverse, and space will not permit enumeration except of a summary nature. Much of the longer fiber is spun into yarn, which is woven into such fabrics as brake linings, tape and cloth. The cloth may be used for various purposes, including brake linings, gaskets, theater curtains, insulating mats, awnings, aprons and gloves. Explorers that have descended into the craters of active volcanoes have worn asbestos clothing.

A portion of the longer grades is used as wick and rope packings, filling for mattress insulation, and substantial quantities in magnesia-block insulation, consisting of 85 per cent magnesia and 15 per cent asbestos.

The fact that it is the only fibrous mineral binder accounts for many uses where asbestos aids in holding together and reinforcing cement products, plasters, asphalt, and molded articles of the cold-molded and bitumen type, and those made with synthetic resins of the phenolformaldehyde type.

Shingles, siding, and other forms of asbestos lumber are made from medium-length grades of fiber by mixing with cement. Asbestos tile

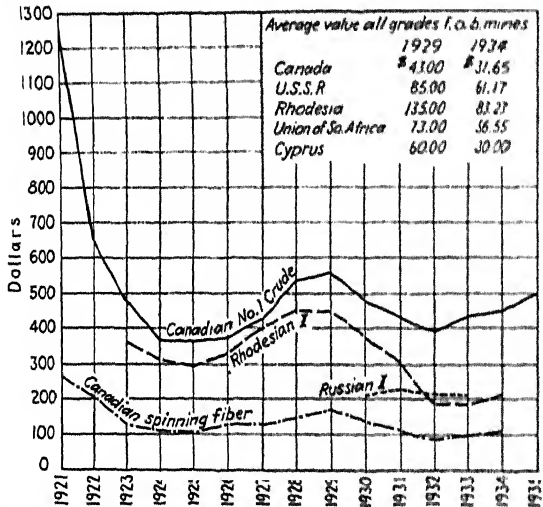


FIG. 3.—YEARLY AVERAGE VALUE PER SHORT TON OF CANADIAN NO. 1 CRUDE AND SPINNING FIBER.

Sales prices f.o.b. mines. Rhodesian I and Russian I. Quotations c.i.f. European ports.

piping and conduit are also of this class. These grades also are processed with rubber in the manufacture of sheet packing and associated products including certain kinds of brake lining.

Paper stock, as the name applies, is used largely in the manufacture of asbestos paper. Much of this is made into air-cell and other types of boiler and pipe covering. The development of molded brake lining and clutch facing, which are made from heavy paper of the millboard variety impregnated with certain compounds, has created additional demand for these fibers at the expense of the spinning grades.

Asbestos cement, widely used for boiler insulation, is made from the waste or plaster grades. These and refuse or shorts are constituents of cold-molded and synthetic resin products, various kinds of flooring, as filler in paints and greases, and of other compositions.

The many uses for which asbestos is so peculiarly adapted make it invaluable to industry. No single substance combines the variety of

properties that this does; it withstands fire and insulates against heat and sound; it is light in weight, and can be made into pliable fabrics; it resists soil corrosion and the attack of vermin. Uses are ever expanding and undoubtedly it will continue to play a prominent part in the development of transportation, building, and other industries.

Prices of the various fiber grades cover a considerable range. Floats and other very short grades sell down to \$10 and less per ton; cement stocks from \$20 to \$25; paper stock from \$30 to \$40; shingle fibers range from \$45 to \$65; and spinning fibers are generally something over \$100 per ton. Prices for Canadian crudes, for the last 10 years, have averaged about \$450 per ton for No. 1 and something less than \$250 for No. 2. Early in 1921 quotations for No. 1 crude reached a high of more than \$3000 and three years later had a quoted low of \$300 per ton. The prices for shorter fibers fluctuated less violently, but shingle stock sold for over \$100 in 1921.

The graph of Fig. 3 shows average values based on yearly sales for Canadian No. 1 crude and spinning fiber, while the Rhodesian I and Russian I are plotted from average price quotations, according to statistics published by the Quebec Bureau of Mines.

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## BARIUM MINERALS

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ONLY two minerals of barium are produced commercially—barite ( $\text{BaSO}_4$ ) and witherite ( $\text{BaCO}_3$ ). Barite is also called “baryta,” “barytes” and “heavy spar,” and locally in Missouri, “tiff.” Witherite sometimes is also called “heavy spar.” More often it is simply called barium carbonate.

Pure barite is white opaque to transparent. Impurities sometimes give pale shades of yellow, green, blue, brown, red or gray-black to black. Barite crystallizes in the orthorhombic system. Twinning is common. The fracture is uneven and the mineral is brittle. Hardness varies from 2.5 to 3.5 and specific gravity from 4.3 to 4.6. Different localities are known to produce either “hard” or “soft” barite. The soft variety is more desirable for grinding. The streak is white. The luster is pearly to vitreous or sometimes stony. Theoretically barite contains 65.7 per cent  $\text{BaO}$  and 34.3 per cent  $\text{SO}_3$ .

Witherite is white, gray or yellow. It is transparent to translucent to opaque. The streak is white. It crystallizes in the orthorhombic system. It is brittle with uneven fracture. The hardness varies from 3 to 3.75 and the specific gravity from 4.29 to 4.35. It effervesces with cold dilute hydrochloric acid as distinguished from barite. Its theoretical composition is  $\text{BaO}$ , 77.7 per cent;  $\text{CO}_2$ , 22.3 per cent.

## ORIGIN AND MODE OF OCCURRENCE

Barite deposits, according to their mode of occurrence, may be loosely grouped under three classes:

1. Those in which barite is a gangue or accessory mineral in metaliferous deposits.
2. Veins, replacements or breccia filling in sandstones, shales, limestones or crystalline rocks. Replacements sometimes occur as bedded deposits due to the complete replacement of sedimentary beds.
3. Residual deposits in clays, derived from the weathering of barium-bearing rocks. The most typical of these are the residual deposits resulting from the weathering of Cambrian or Ordovician dolomites.

Deposits of the first class have but little economic importance as far as the barite is concerned, it being usually difficult or impossible economically to separate a barite product of standard commercial grade.

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Deposits of the second class constitute an important economic group and are the source of production in some localities. They are also the source from which the third class is derived. The third group is of the greatest economic importance in the United States, as it includes the principal producing fields of Missouri, Georgia and Tennessee. Deposits of the second class are found in rocks of practically all ages from Archean<sup>11</sup> to Mesozoic.<sup>5</sup> Most of the commercial deposits of this class are in limestone or dolomite, but a few are in the crystalline rocks.

*Fissure Veins, Replacements and Breccias.*—In the Hot Springs and Kings Mountain area of North Carolina the veins are irregular in shape, varying from a few inches to 18 ft. wide.<sup>11</sup> The enclosing rocks are granites of Archean age, feldspathic quartzites of Cambrian age and fine-grained, white, siliceous sericite schist of Algonkian age. Barite veins in the Appalachian Valley of Virginia occur in Beekmantown (Lower Ordovician) limestones and dolomites. Calcite, quartz and pyrite are associated minerals. Some fluorite is nearly always present. In the Piedmont province of Virginia the veins are in pre-Cambrian crystalline rocks. The associated minerals tourmaline, hornblende, biotite, epidote and chlorite are thought to be distinctive of these deposits.<sup>5</sup> Barite veins in the central part of Kentucky are simple fissure or fault fractures in Ordovician limestone. The associated minerals are calcite, fluorite, galena and sphalerite. Barite occurs with fluorite in nearly vertical veins in Mississippian limestone in the western part of the state.<sup>9</sup> Strong veins of barite occur in Carboniferous rocks west of Boulder, Colo. Near El Portal, Mariposa County, Calif., the barite occurs as lenses, averaging 14 ft. with a maximum of 35 ft., in a vein of varying width. Both barite and witherite are found in this deposit.<sup>2</sup> At Lake Ainslie, Cape Breton, Canada, barite associated with calcite and fluorite occurs in veins in pre-Cambrian felsite. Near Five Islands, Nova Scotia, fissure veins and brecciated zones are found in Devonian slates and quartzites.

Replacement deposits are sometimes associated with veins, especially in sedimentary rocks. They usually show gradational boundaries in true replacements and sometimes merge into filled breccias where some of the brecciated fragments have been partly replaced with barite. Edmundson<sup>5</sup> says that in Virginia they are in the form of lenticular bodies, sometimes up to 20 ft. in diameter and are best developed in limestone and marble.

A replacement of shale by barite occurs in central Arkansas.<sup>1</sup> The deposit has replaced shale beds at the base of the Stanley formation of Mississippian age. It lies on the north flank of a steep synclinal valley, the west end of which contacts the igneous rocks of Magnet Cove, about  $1\frac{1}{2}$  miles distant. The known thickness is 44 ft. normal to the bedding plane. The bedding planes have been preserved in the replacement.

<sup>11</sup> References are at the end of the paper.

Replacement deposits of barite in Carboniferous limestone occur in Belgium. Near Meggen, Westphalia, a bituminous barite is supposed to have replaced portions of a bedded Devonian pyrite, which in turn grades into limestone.<sup>9</sup>

Some breccia deposits resemble veins and are often associated with them. They are the result of the filling of the voids in the original brecciated zone rather than a clear-cut single fissure or fault, as with a vein deposit. Few of them are of economic importance in themselves but the barite in some of the residual deposits may be the result of the weathering of barite-filled breccias.

*Residual Deposits.*—By far the greatest production of barite in the United States is from residual deposits formed by the weathering and disintegration of rocks in which the barite was originally deposited in the form of veins or breccias. Probably few of them are the result of the weathering of replacements.

The residual deposits of southeastern Missouri are found in the clay mantle covering the underlying dolomites. These dolomites originally contained the barite in the form of veins or breccia fillings and the weathering of the rock left the less soluble barite in the residual clays. The dolomites are of Cambrian age. Deposits on the Potosi formation of the Cambrian are the most important but the overlying Eminence formation accounts for some. The deposits consist of loose fragments of barite, with chert, drusy quartz and boulders of dolomite and sandstone embedded in the red clay. There is often a concentration of the larger fragments near the bottom or even on bedrock. The clay mantle varies from 0 to 30 ft. thick. Areas of 100 acres or more may be ore-bearing but there is usually a concentration of the barite in runs or "leads" 10 to 20 ft. wide and several hundred feet long. A typical section is as follows:<sup>14</sup>

Surface soil.....	1 ft. to 1 ft. 6 in.
Chert, gravel and clay.....	1 ft. 6 in. to 2 ft.
Clay, barite, chert and drusy quartz, barite in small fragments, not over 2 in.....	2 ft. 6 in. to 4 ft.
Practically barren, dark red clay.....	3 ft. to 4 ft.
Red clay, large chert and dolomite boulders and large masses of barite, sometimes in almost continuous sheets 4 to 6 in. thick and several square feet horizontal extent	1 ft. to 2 ft. 6 in.
Red clay, practically barren, depth to bedrock not exposed.	

The barite is pure white on a fresh fracture, although the surfaces and cleavage planes are usually coated with a thin film or stain of limonite. The larger lumps often have deep cavities on their surfaces lined with a layer of hard limonite  $\frac{1}{32}$  to  $\frac{1}{16}$  in. thick. Massive galena is sometimes associated with the barite.

In the central Missouri district the residual deposits are often found in clays on top of the weathered surface of the Gasconade formation, the

top member of the Cambrian, but sometimes on the Roubidoux, the bottom of the Ordovician, or near the contact of these two. The mode of occurrence is much the same as in southeastern Missouri except that the deposits are deeper and of very restricted horizontal extent. The barite is a harder variety and is less stained and coated with limonite. Drusy quartz is absent. These deposits are probably more often the remains of filled breccia deposits than of fissure veins.

The residual deposits of Virginia have been the source of most of the production from that state. In the Piedmont region barite is found in red to black clay, the remains of the weathering of limestone and mica schist of Cambrian and pre-Cambrian age. In some places ocher and umber of commercial grade is associated with the barite, as are also manganese oxides. In the Valley region the enclosing clays were derived from the Knox dolomite.

In the residual deposits near Cartersville, Ga., the barite occurs as pebbles, nodules and masses embedded in the residual clays derived from the weathering of the Weisner quartzite and shaly limestone of the Beaver formation overlying it. These are the two lower formations of the Cambrian. The barite originally was deposited in fractures and cavities in these rocks. Some of it was possibly a replacement of part of the limestone. In the upper part of the deposits, on the slopes of the hills, concentrations of iron ore rest directly on the quartzite. The barite occurs below this on the slope with a rather sharp line of division between. The barite and its enclosing clay is usually underlain by remnants of the lower beds of the limestone, which have been completely weathered under the iron ore.

The residual deposits near Sweetwater, eastern Tennessee, are in clays averaging 10 to 20 ft. thick but occasionally reaching a thickness of 60 ft. These clays cover the Knox dolomite of Cambro-Ordovician age. The barite is of both the hard crystalline and soft varieties. It is iron-stained and sometimes coated with a hard layer of limonite.

*Origin.*—Clarke states<sup>3</sup> that most of the occurrences of barite and witherite indicate minerals of aqueous origin. This refers to deposits of barite in place in veins, breccias and replacements. It is generally accepted as a fact that the barite in residual clay deposits is the accumulation of the barite in bedrock deposits caused by the weathering of the enclosing rocks.

There are two schools of thought on the source or origin of the barium in the mineralizing solutions from which it was deposited in the various types of deposits found in place. One holds that most of the deposits were derived from descending meteoric waters and the other that they were deposited from magmatic or ascending waters. In either case the original source of the barium was in the igneous or crystalline rocks. If the meteoric waters theory is adhered to, the weathering of these rocks

permitted the barium compounds to be deposited along with the sedimentaries resulting from the remains of the weathering or erosion of the original rock. From this position the barium was picked up in solution by descending or circulating meteoric waters and deposited or precipitated from these mineralized solutions in veins, breccias or as replacements in adjacent or underlying formations where conditions were favorable. The chemistry of the process is explainable. In some deposits the points in favor of meteoric origin are sound and difficult to refute. For example, there may be no igneous rocks in near association with the deposit. Some of the associated minerals are known to occur in deposits formed by meteoric waters, which are rarely found in deposits of magmatic origin. There is often no alteration of wall rocks such as would be expected if they were subjected to hydrothermal action. If the deposits are due to magmatic waters these would have taken up their barium compounds from deep-seated igneous rocks or from intrusives or other rocks affording a source of the barium. These mineralized solutions, then, in ascending deposited the barite where conditions of rock structure, temperature and chemical action were favorable. In some deposits the evidence in favor of magmatic origin seems quite conclusive, such as silicification of the wall rocks, association of minerals of definite hydrothermal origin, close association of igneous or intrusive rocks, lack of sufficient barium in surrounding or overlying formations to afford the amount of barium present in the deposit, and lack of evidence of solution or leaching of adjacent rocks.

The various deposits of the world show such a diversity of occurrence that examples can be cited in which the evidence in favor of each theory is strong. It is probable that barite deposits have been formed by both processes.

#### DISTRIBUTION OF DEPOSITS

Deposits of barite occur in all parts of the world. This wide distribution, coupled with the fact that low-priced substitutes for many of its uses are available, reacts to keep it a comparatively low-priced commodity. For this reason development has taken place only where a market is readily available, mining costs are low and low-cost transportation is near at hand.

*United States.*—Deposits in the United States that have produced recently are principally as follows. Near Cartersville, Ga., is one of the most important districts. The North Carolina deposits are near Hot Springs and Kings Mountain. The Kings Mountain district extends southwestward into South Carolina and at one time was developed at Kings Creek, Cherokee County. Barite occurs in Virginia in 19 counties. The two most important areas are in the southwestern and central southern part of the state. In Kentucky there are many vein deposits in the

central part of the state near Lexington, but production has never been large. There are also deposits in the western part of the state. The Tennessee deposits, near Sweetwater, are of very considerable commercial importance. Alabama was a producer up to a few years ago. In Missouri, the state with the greatest production, the principal area is in Washington County, in the southeastern part of the state, with deposits of lesser importance in the central area southwest of Jefferson City. Deposits near Canon City and Boulder, Colo., have accounted for small production at various times. Producing veins in California are in Mariposa, Nevada and Shasta Counties. The mine at El Portal, Mariposa County, is the only producer of witherite in the United States. It also produces barite. A deposit on the west coast of Prince of Wales Island, Alaska, was at one time a small producer. Small amounts of barite have been produced at intervals in Esmeralda and Mineral Counties, Nevada, Sierra and Dona Ana Counties, New Mexico, Lafayette County, Wisconsin, and Blaine County, Idaho. Deposits have also been noted in Connecticut. A large undeveloped deposit is near Magnet Cove, Ark. The Llano district, in central Texas, is reported to have possible economic deposits.

*Foreign.*—Many foreign countries have deposits of barite, but Germany, Italy, Canada, Great Britain and Russia are the principal ones with commercial production entering into world trade. Spain produces some barite, some of which is exported. Germany's most important deposits are in the Thuringian Forest, the Black Forest, the Odenwald, Hesse and the Bavarian Palatinate. In Italy the principal producing districts are Carrara, Iglosias, Milano and Trento. Canada's principal commercial deposits are on Lake Ainslee, Nova Scotia. Other deposits, which have accounted for a small production, are in Ontario.<sup>10</sup>

England has been the chief producer of witherite. The deposits are in Northumberland County, in the north of England. Deposits of barite are developed in Northumberland, Durham, Cumberland, Westmoreland and Yorkshire Counties. Deposits of barite are noted in other parts of England. Deposits in Scotland are commercial producers.

Russia has entered the field of producers within the past few years. Deposits are reported at numerous localities. High-grade concentrates are produced at Salair, U. S. S. R.<sup>4</sup> Undeveloped deposits are reported in western Siberia, the larger of which is near Askyskom. Others are in the region of Morozoc Ulus, and at Chapsordag and Taptan-Tursy in the Hakassia district. There are producing mines in Georgia and Azerbaidzhan. New deposits are reported in the Urak, Siberia, Karelia, the North Caucasus and Central Asia.<sup>5</sup>

#### POLITICAL AND COMMERCIAL CONTROL

Most of the principal consuming countries of the world have sufficient supplies of barite for their own use. There is, however, some interna-

tional flow of crude or ground barite. This movement is based more on final cost at the point of consumption than on origin, source of supply or national boundaries. Factors entering into this are cost of mining and dressing or concentrating, transportation, tariffs, and grade of product. For example, the United States has ample reserves and potential production to take care of all its needs, yet a considerable tonnage is imported for consumption along the Atlantic seaboard because the delivered price is lower than that of domestic barite from the principal fields in Georgia and Missouri, owing to lower European production costs and low ocean rates compared with high American labor costs and higher rail rates.

The United States and Germany are the two largest producers. In 1931 and 1932 the United States production exceeded that of Germany. In 1933 and 1934 German production exceeded that of the United States. During the past few years Russia has become a factor in world trade. In 1913 Russia was an importer, while now it exports considerable amounts. The first exportation to the United States was in 1931. Outside of Russia's entrance into the world markets, there has been little change in the political control within the past few years, except some fluctuation in imports and exports of the principal countries. German exportation to the United States has decreased greatly and that from Spain has increased sharply. These fluctuations have been controlled probably more by trade balances and monetary exchange than by actual supply and demand.

The United States tariff law of 1930 provides a duty of \$4 per ton on crude barite and \$7.50 per ton on ground or otherwise manufactured.

#### PRODUCTION AND CONSUMPTION

Barite production in the United States started in Virginia about 1845. Production in Missouri began about 1860. European production probably began many years before it did in the United States. Many of the present uses for barite were unknown during the earlier years of production, hence the output necessary to meet the demand was small and variable. A gradual expansion of markets and a better knowledge of the chemical and physical properties of the mineral caused production to increase slowly. In the past 25 years consumption followed by production has advanced more rapidly. The United States, Germany and Great Britain are the principal producing countries. In some years German production exceeds that of the United States.

Fig. 1 shows graphically the gradual upward trend of production for the last 14 years if an average is considered, and the peaks and depressions balanced against each other. United States imports are also shown.

#### PROSPECTING, EXPLORATION AND MINING METHODS

Prospecting for barite is a rather simple and inexpensive operation. After the district where barite is known to occur has been explored in a

general way, the most favorable areas are selected for prospecting. Two methods are employed for residual deposits. In Missouri the choice is largely based on topography. A slender, pointed steel rod is driven into the ground, to bedrock if possible. If the rod penetrates barite the soft white mineral adheres to the rod when it is withdrawn. Chert and rock, if encountered, only scratch the rod without leaving a white coating. Test pits are sometimes sunk following the "rodding." In the Georgia (U. S.) residual deposits the practice is to sink test pits of circular section. The clay overburden stands very well without cribbing and the pits are often sunk to a depth of 30 ft. or more. They are only large enough for

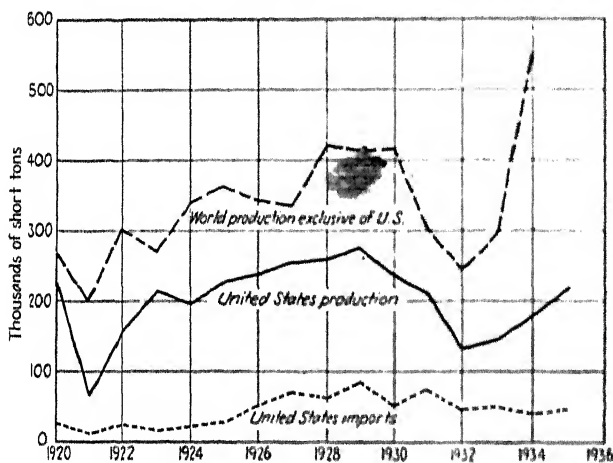


FIG. 1.—PRODUCTION OF CRUDE BARITE.

one man to work in with a short-handled pick and shovel. The excavated material is hoisted out by one man on the surface.

The prospecting of vein deposits is done in the usual way by trenching across the vein outcrop, sinking prospect shafts and tunneling when the topography permits. Elaborate and expensive methods such as diamond drilling are seldom resorted to.

**Mining Methods.**—Most of the United States production is from residual deposits, so the methods employed for these operations are of first importance. When labor is plentiful and low priced, hand mining is adopted. When it is scarce and higher priced, mechanical methods account for a greater amount. In the Missouri district both hand mining and mechanical or power-shovel mining are employed in working the residual deposits.

When barite is mined from veins or deposits in solid rock, the usual methods for such deposits are employed. The system employed depends on the topography, character of the wall rock, thickness and dip of the vein and the kind and amount of the associated minerals. Vein mining of minerals in hard rock has been fully described in other chapters.



*Hand Mining.*—The hand miner's or "tiff digger's" tools consist of a pick, shovel, sledge, small hammer with one end finished with a blade like a hatchet or chisel, hand windlass, rope, and ore bucket and an axe.

On the allotted area previously prospected, a pit or shaft is started where it is believed the best barite will be found. This shaft is  $4\frac{1}{2}$  to 5 ft. in diameter, usually circular, unless it has to be cribbed. The dirt is thrown out until the shaft becomes too deep. Many pits never go deeper. On the surface the dirt is worked over by pick and shovel and the lump barite picked out by hand and piled separately. The larger lumps are cleaned of clay with the aid of a hatchet or edge-faced hammer. When a good run of ore is struck, it is followed out horizontally as far as possible, until there is danger of the walls and roof caving in. Thus, in section, the shaft and excavation has the shape of an inverted mushroom. Occasionally the shafts reach a depth of 30 to 40 ft., but 10 to 15 ft. is more common. When the depth requires a windlass two or three men work together, one in the pit and one or two on the surface, hoisting and sorting. When one pit is worked out, another close by, often within 10 to 12 ft. of the other, is started and worked out in the same way.

Hand mining methods are best adapted to areas where the barite occurs in large masses or lumps and where the surface of the bedrock is uneven, making clean excavation with a power shovel difficult. The miner is invariably paid on a tonnage basis of barite recovered and cleaned.

In the central Missouri district, where the deposits are often on steeper hillsides, and deeper, the mining is done in open cuts with a level floor. The face of the bank is broken down by picks or barring from above. Sorting is done on the open-cut floor and the barite and clay are hauled out separately. Large boulders are left in place and mined around.

*Mechanical Methods.*—Mining with power shovels is sometimes done in Missouri where the deposit covers a fairly large area on gently sloping ground and where the surface of the bedrock is not too irregular or does not have many deep, narrow depressions. Areas previously worked over by hand are sometimes again excavated by a power shovel. Shovels are mounted on caterpillar treads and are of the full revolving type. Dippers are from  $\frac{3}{4}$  to  $1\frac{1}{2}$  cu. yd. in capacity. Gasoline or semi-Diesel engines are most common, but steam and electric are also used.

In excavating, the full depth of the deposit is taken at one cut and no overburden is previously stripped. The dirt is loaded into side-dump cars of about 5-yd. capacity and hauled to the washing plant by gasoline locomotives. On account of the uneven surface of the bedrock it is impossible for a power shovel to remove all the ore from the depressions. Where these are deep enough and frequent enough they are sometimes mined by hand after the shovel has worked over them.

In Georgia all mining is done with power shovels. The deposits are thicker than in Missouri and the slopes of the hill generally greater.

Sometimes the overburden is thick enough to remove and dispose of separately. If thin, it is excavated with the ore and sent to the washer. Adjacent deposits are sometimes connected by narrow stringers of pay dirt, permitting the shovel to cut through and follow from one to the other. Shovels are equipped with  $\frac{3}{4}$  to 1-yd. dippers. These load into small cars for haulage to the washer. Blasting of the face is sometimes resorted to where the bank is high, to prevent overhanging followed by possible caving and burying of the shovel.

#### PREPARATION FOR MARKET TESTS AND SPECIFICATIONS

Barite is sold or marketed in the form of crude lumps, jigged concentrates or table concentrates. Lump ore may be prepared from residual deposits or from vein deposits. It is essentially a product of hand sorting. With ore from veins the waste rock or gangue is sorted out with possibly some hand cobbing, either on platforms or picking belts. In one California mine where witherite occurs with the barite, the two minerals are sorted or separated by hand. Hand-mined ore from residual deposits, as in Missouri, is piled in the open to weather. The adhering clay dries, shrinks and falls loose from the barite or is scraped or chopped off with a hatchetlike tool. After drying the smaller lumps are shoveled into a rocker, a box about 20 in. wide by 32 in. long by 12 in. deep, fitted with a punched-plate or coarse wire screen bottom. The bottom is fitted with rockers, and as the box is rocked back and forth the clay falls through the screen. The screened barite and hand-cleaned lumps are then ready to haul to the nearest shipping point. Where the clay separates readily from the barite, the rocker is not used. After weathering, the operation of handling or loading with a fork into wagons or trucks, and again forking as loaded into railroad cars, removes the clay to the necessary limit.

Jigged and tabled barite concentrates are produced both from vein and residual deposits. Where there is no adhering or associated clay, standard practice for gravity concentration is practiced. With residual ores where most of the waste or gangue is clay, the jigging and tabling is always preceded by treatment in a log washer. Hand picking of the coarse, clean barite after passing through the log washer, is also practiced in some districts, notably Georgia.

A generalized flowsheet of modern practice in the Georgia field is shown in Fig. 2. This varies in detail to suit local conditions. For example, a jaw crusher may take the rake product of the log washer ahead of the coarse screen. However, there are usually very few compound or locked mineral grains or fragments in residual barite deposits, and these are usually broken up in the revolving coarse screen, as the barite is very friable. Barite washers usually have a capacity of 50 to 70 tons of "dirt" per hour. Of this often 75 per cent will be eliminated by the log washer in the first operation. Grizzly bars are usually placed 6 in. apart. Boulders

too large to pass are broken by hand or are thrown out if barren. Double washers 30 ft. long are almost standard size. The type and size of the jigs vary with conditions. The same remark applies to tables. There is a tendency towards the use of more tables in the Missouri district to prepare special grades of fine concentrates.

Most barite ores present no especially difficult dressing problems. Some residual ores, where the barite is coated with a layer of hard limo-

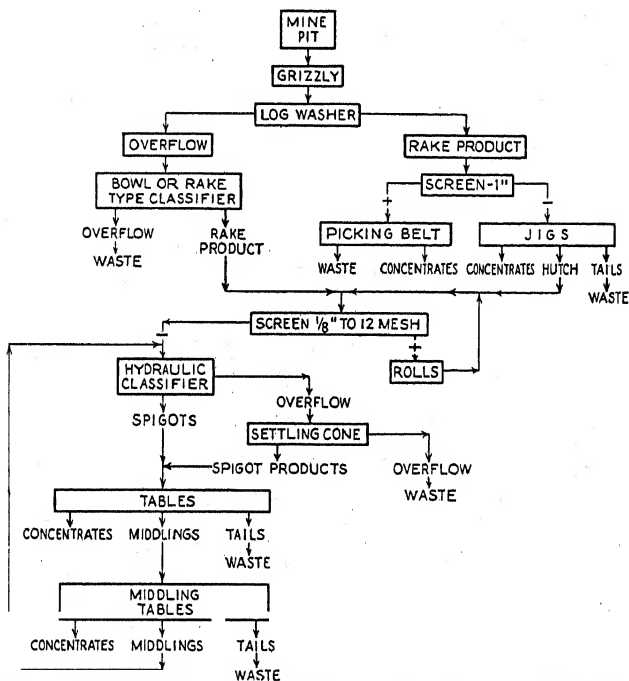


FIG. 2.—GENERALIZED FLOWSHEET, GEORGIA BARIUM CONCENTRATOR.

nite, present a problem because the removal of the coating by gravity methods is very difficult, as the gravity of the two minerals is close. Pyrite and sphalerite are difficult to separate by gravity methods. Galena is easily removed.

*Special Treatments.*—When the removal of limonite is essential, the limonite is sometimes removed by roasting and separation on a high-intensity magnetic separator. Another method is to leach the granular material, 14-mesh or finer, with dilute sulphuric acid. This does not completely bleach the barite but may lower the iron content sufficiently to meet special specifications for use in glass. In one operation in east Tennessee, where the limonite coating is excessive, the barite is crushed to a size larger than the granular product required and then calcined in a small rotary furnace. This causes the barite to decrepitate or break down without altering the size of the limonite grains. Then a fair separation

can be made on screens, which pass the finer barite and reject the limonite. In the Missouri district some of the barite is prepared for the glass trade by careful hand selection of hand-mined lumps low in iron. These are then crushed and screened to proper size.

Some barite occurring in veins and replacement deposits is intimately intergrown with quartz or other minerals, making gravity separation practically impossible. Some experimental work indicates that flotation may make a satisfactory concentrate from these ores.<sup>3</sup>

*Tests and Specifications.*—No standard tests or specifications for barite are in use. The most common specification used by a good part of the trade, however, is that the product shall contain 95 per cent  $\text{BaSO}_4$  and not over 1 per cent  $\text{Fe}_2\text{O}_3$ . A penalty is usually imposed if the ferric oxide exceeds 1 per cent and a premium allowed if it is lower. A premium is sometimes specified for a barium sulphate content in excess of 95 per cent. Purchase orders usually specify the size of the product and whether the barite is to be of the soft or hard variety. Barite for the glass trade is usually specified to contain not more than 0.1 per cent  $\text{Fe}_2\text{O}_3$ , not less than 96 per cent  $\text{BaSO}_4$  and to be crushed to pass a 16-mesh screen with not more than 5 per cent passing 100 mesh. This seems to be an arbitrary requirement, as some of the glass manufacturers are now asking for and taking a finely ground product.

#### MARKETING, USES AND PRICES

*Markets.*—The market outlet for crude barite or concentrates may be grouped under three general heads: (1) ground barite of various grades, (2) lithopone and (3) barium chemicals. The principal processing areas are in the Eastern States, Central States and California. All these areas consume barite for the three general uses mentioned. Some barite is also ground in South Carolina and Georgia. The producing districts of Georgia and east Tennessee market their barite largely on the Atlantic seaboard and in the Eastern States. Some of it moves north of the Ohio River. Imports are largely confined to the Atlantic seaboard. The Missouri barite is largely marketed in the North Central States, the St. Louis district and as far east as Pennsylvania. California production is mostly consumed or processed in California. This distribution of markets is largely controlled by transportation conditions.

Some of the largest consumers or processors of barite have their own mines, hence much of the production does not come into the competitive market. Most of the crude barite sold is marketed to consumers on the basis of contracts for a particular tonnage to be shipped over a definite period of time. A large producer may not be in the market for some time and then may place a contract for several thousand tons at one time, to supply his needs for several months. Minimum barium sulphate content and maximum iron oxide content are always specified. On some shipments the grain size is also specified.

*Uses.*—During the five-year period 1930–1934, of the total crude barite processed, amounting to  $1\frac{1}{4}$  million tons, both domestic production and imports, 19.1 per cent was ground, 58.2 per cent was used in lithopone and 22.7 per cent was used for the manufacture of barium chemicals.

Barite ground to various degrees of fineness is used as an inert filler in many products such as rubber, paper, oilcloth, plastics and resins. It is also used to weight textiles and leather. To some products it adds desirable properties. In others its function is mainly for weight and volume. All grades are used, from an off-color product to a white, acid-bleached one. Ground barite is also used in paint as a pigment and as an extender. A comparatively recent and important use is as a heavy medium in mud used in the drilling of deep oil wells where there are heavy gas pressures. A small amount of some suspending medium such as bentonite is often added to and ground with the barite. The use of barite for this purpose is covered by broad and comprehensive patents.

Granular barite, classed here under “ground,” is finding extensive use in the manufacture of glass. Small amounts added to the glass mix add desirable properties to some grades of glass, especially the molded forms. A low iron content is essential. Barite is used to some extent as a flux in brass melting, its function being mostly as a scavenger. It has also been proposed as a flux in the founding of gray iron.

Barite’s greatest single use is in the manufacture of lithopone. This is an intimate mixture of zinc sulphide and barium sulphate made by the coprecipitation of solutions of barium sulphide and zinc sulphate. It is mainly used as a white paint pigment but also finds considerable use as a filler. It contains approximately 70 per cent barium sulphate and 30 per cent zinc sulphide.

Barite is the raw material for the manufacture of most barium chemicals, although witherite is used when available. The initial step is the furnace reduction, with carbon to the soluble barium sulphide, known as “black ash,” or with calcium chloride to produce barium chloride. The principal barium chemical made is precipitated barium sulphate or *blanc fixe*. This is a whiter and finer grained product than it is possible to make mechanically from the natural barite. It is used as a filler, in paints and for special purposes. Precipitated barium carbonate is used in the ceramic industry and for making barium peroxide. Other important barium chemicals are the nitrate, chloride, hydrate, dioxide, peroxide, chromate and chlorate. Small amounts of metallic barium are used in some special alloys.

*Prices.*—Barite has always been and probably always will be a low-priced commodity, because of its wide distribution, ease of mining and concentrating, and because for many of its uses it is in direct competition with other low-priced minerals. Except for a few minor uses, it is not indispensable. Prices at point of production are governed largely by

cost of transportation to the marketing centers. The fluctuations in and the gradual upward trend of price as uses have expanded in the 30-year

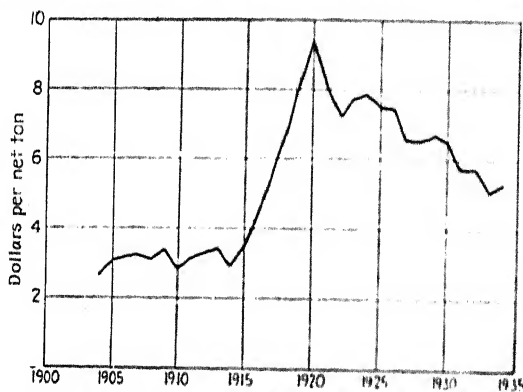


FIG. 3. PRICE OF CRUDE BARITE, F.O.B. MINE

period 1904–1934 are shown graphically in Fig. 3, plotted from statistics by the U. S. Geological Survey and U. S. Bureau of Mines.<sup>7</sup>

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## BAUXITE\*

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**B**AUXITE is known mainly as the ore from which aluminum is smelted, but it has large use also in the manufacture of artificial abrasives and as a basis for certain chemical industries. A small amount is used for refractories and for other purposes.

## COMPOSITION AND PROPERTIES

*Composition.*—Dana and others give the mineral formula of bauxite as  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , and the composition  $\text{Al}_2\text{O}_3$ , 73.9 per cent;  $\text{H}_2\text{O}$ , 26.1 per cent. It has been definitely shown, however, that bauxite does not exist as a specific mineral but rather as a rock. The term is now used synonymously with aluminum ore and it embraces gibbsite (hydrargillite or alpha trihydrate),  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  ( $\text{Al}_2\text{O}_3$ , 65.4 per cent;  $\text{H}_2\text{O}$ , 34.6 per cent); boehmite (alpha monohydrate),  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  ( $\text{Al}_2\text{O}_3$ , 85 per cent;  $\text{H}_2\text{O}$ , 15 per cent), diasporite (beta monohydrate),  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  ( $\text{Al}_2\text{O}_3$ , 85 per cent;  $\text{H}_2\text{O}$ , 15 per cent) and mixtures in various proportions of any two of them. Bauxite of the Mesozoic and Tertiary in Europe is predominantly a mixture of gibbsite and boehmite, subordinately a mixture of boehmite and diasporite, or gibbsite and diasporite. The bauxite of North and South America, tropical Africa and Asia, consists largely of gibbsite. Corundum ( $\text{Al}_2\text{O}_3$ ) is not included under bauxite, although gradations from bauxite to emery or corundum exist.

All bauxite, irrespective of the aluminum minerals composing it, contains certain impurities, including silica, in the form of clay minerals (kaolinite, halloysite, etc.) or quartz, iron oxide (as hematite or goethite), titania (as leucosene or rutile), iron sulphide (as pyrite or marcasite), iron carbonate (siderite), and calcium carbonate (as calcite); the last three mentioned in minor amount and of local occurrence only. Bauxite belongs to a group of partly consolidated materials called laterites, formed by surface weathering. This group includes also impure siliceous and ferruginous bauxite and siliceous and aluminous iron ores and manganese ores.

\* Through the courtesy of the McGraw-Hill Book Co. much of this article was abstracted from the chapter on Ores of Aluminum, by E. C. Harder, in *The Aluminum Industry*, by J. D. Edwards, F. C. Frary and Z. Jeffries, New York, 1930. Other references are given in the bibliography at the end of this chapter.

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*Properties.*—Gibbsite is white or light shades of gray, cream or pink. Its hardness is 2.5 to 3.5; specific gravity, 2.3 to 2.4; crystal system, monoclinic, crystals tabular parallel to 001, often fibrous, concretionary, stalactitic; luster, vitreous to pearly; generally translucent; cleavage, parallel to 001; disassociation temperature, approximately 300° C.

Boehmite, a new mineral described by J. Boehm in 1925, confirmed and named by J. de Lapparent in 1930, has some properties not yet definitely determined. It occurs in grayish, brownish and reddish shades. Its hardness is between that of gibbsite and diaspore; specific gravity, similar to diaspore; crystal system, orthorhombic, best developed along 110 and 001; angle between the faces *m* near 63°; cleavage, parallel to 010; X-ray pattern distinctly different from that of diaspore.

Diaspore is white or light shades of gray or brown. Its hardness is 6.5 to 7; specific gravity, 3.3 to 3.5; crystal system, orthorhombic, crystals prismatic, flattened, parallel to 010; luster, pearly to vitreous; transparent to translucent; birefringence high; cleavage, parallel to 010; disassociation temperature approximately 500° C.

Bauxite as it occurs in nature rarely exhibits the distinct characteristics of its constituent minerals. These become apparent only by examination of thin section under the microscope, by the determination of heating curves, by chemical analysis or by X-ray tests. Not all the constituents in bauxite are recognizable even by such methods and it is therefore believed that much of the alumina is present in the form of colloidal hydrogels, with a variable combined water content. Bauxite is a medium soft to hard rock, has a fine-grained cellular, porous or compact structure, a conchoidal or uneven fracture and ranges in color from light gray, cream, pink or yellow to dark brown and dark red. In many localities the bauxite is characterized by an oolitic or pisolitic texture, the oolites ranging in size from less than  $\frac{1}{20}$  in. to  $\frac{1}{2}$  in. or more. The oolites may have a concentric texture or they may be homogeneous. Small oolites may occur grouped together within larger ones. The color of the oolites generally differs somewhat from that of the matrix—usually, but not always, being darker. There is much bauxite that does not show oolitic texture but has an even-grained, homogeneous or claylike appearance. Some is porous or cellular. In many places oolitic and nonoolitic bauxite occur together in the same deposit.

#### MODE OF OCCURRENCE

Bauxite deposits occur in a number of different geologic associations but most of them can be grouped into four main classes:

1. Blanket deposits occurring at or near the surface in horizontal, tilted, or undulating sheets and lenses.
2. Beds and lenslike deposits occurring at definite stratigraphic horizons interlayered with sediments or between sediments and igneous rocks.



3. Pocket deposits or irregular masses enclosed within limestone or clay.

4. Detrital deposits formed by the mechanical breaking up, transportation and redeposition of the material from deposits of the other three types.

These four types of deposits are closely related to each other and are in many cases gradational. There is a strong possibility that the first three have a somewhat similar origin.

The table on page 114 shows the general age relations of the principal bauxite deposits of the world.

*Blanket Deposits.*—Horizontal blanket deposits of bauxite or laterite are commonly found in tropical or semitropical regions, where they occur on base-leveled surfaces. Some of them are at low elevations and others occur as cappings on extensive plateaus or on flat-topped hills representing outliers or remnants of such plateaus. The elevated bauxite-bearing plateaus are former base-leveled surfaces that have been raised and subjected to erosion subsequent to the original peneplanation and formation of bauxite. In many places the laterite or bauxite deposits are at the surface, covered only by sparse vegetation; elsewhere, varying thicknesses of soil cover them. Generally the surface and upper portion of the deposits is hard and indurated owing to infiltration and cementation by iron oxide or siliceous material. With depth, it becomes softer and at the bottom it passes rather abruptly into the underlying residual clay. Locally small, irregular pipes or networks of pipes of bauxite project downward into the residual clay from the lower surface of the bauxite layer.

Blanket deposits of bauxite or laterite range in thickness from less than 1 ft. to 75 ft. or more; the average is from perhaps 5 to 25 ft. Horizontally blanket deposits may extend for a few hundred feet or for several miles. The entire layer, except for variations at the immediate surface or at the base, may be fairly uniform and may consist of high-grade bauxite or of siliceous or ferruginous bauxite. On the other hand, however, there may be variations both vertically and horizontally, with the different phases lying in well marked layers or grading into each other laterally or being irregularly intermixed.

*Interlayered Deposits.*—Most layers and lenses of bauxite or laterite interbedded with sediments or lying between sediments and igneous rocks are what might be termed "fossil blanket deposits." They represent surface deposits of past geologic ages that have been submerged subsequent to their formation and have had deposited upon them successive beds of later sediments. As far as texture and composition are concerned, interbedded bauxite deposits in general resemble surface deposits, except that they have a tendency to be harder, more compact and more indurated, owing, no doubt, to the weight of the overlying sediments. They show

*General Age Relations of Principal Bauxite Deposits*

Pleistocene and Recent	Tropical lateritic bauxite of the Guianas, Brazil, French West Africa, Gold Coast, Nyasaland, India, Dutch East Indies, Australia
Cenozoic	
Pliocene	
Miocene	German bauxite (Vogelsberg Mountains)
Oligocene	Irish bauxite (County Antrim)
Eocene	
Upper	
Middle	
Lower	United States bauxite—underlain by lower Eocene or Lower Cretaceous
	Dalmatian bauxite—underlain by lower Eocene and Upper Cretaceous
	Montenegrin bauxite (Bar and Ulcinj)—underlain by Upper Cretaceous
	Istrian bauxite—underlain by Upper Cretaceous
	Spanish bauxite—underlain by Eocene and Rhaetic
	Kashmir deposits (Jammu)—underlain by Jurassic
	Hungarian bauxite—underlain by Rhaetic
Mesozoic	
Cretaceous	
Upper,	
Danian	
Senonian	Greek bauxite—underlain by Jurassic
	French bauxite (Herault)—underlain by Jurassic
Middle,	
Turonian	
Cenomanian	
Albian	Italian bauxite (Central Apennines)
	Montenegrin bauxite (Kotor and Niksic)—underlain by Lower Cretaceous
	French bauxite (Var)—underlain by Urgonian, Neocomian and locally Jurassic
Lower,	
Aptian	
Urgonian	French bauxite (Ariege)—underlain by Jurassic
Neocomian	Rumanian bauxite (Bihar)—underlain by Malm
Jurassic	
Malm	
Dogger	
Lias	
Triassic	
Rhaetic	Croatian bauxite—underlain by Middle Triassic
Keuper	
Middle	
Lower	Chinese diaspora (Poshan)—underlain by "Permo-Carboniferous"
Paleozoic	
Upper Carboniferous	Missouri diaspora—underlain by upper Carboniferous
Lower Carboniferous	Russian bauxite (Tikhvin)—underlain by Devonian
Devonian	Russian bauxite (Ural)—in Middle and Lower Devonian

the same variations in grade, however, and have the same impurities. The overlying rocks may be limestone, shale or sandstone; the underlying rocks may be igneous or sedimentary. In many places rocks with which the bauxite layers and lenses are interstratified have suffered deformation with resultant folding and faulting of the bauxite layers. In places where the deformation has been pronounced, as in parts of France, Rumania and Greece, there has been noted the partial alteration of gibbsite or boehmite to diaspor. Where the deformation has been extreme, as in some of the Aegean Islands, corundum (emery) has developed.

*Pocket Deposits.*—Pocket deposits occur in many places associated with interbedded bauxite layers and lenses. They represent irregularities in the surface upon which the bauxite was formed. In many places bauxite pockets are directly connected with bauxite layers or lenses as extensions from their lower surfaces into pre-existing depressions on the upper surface of the stratigraphically underlying rock, commonly limestone, but in places clay. Elsewhere, pockets are scattered irregularly or occur in groups unconnected with bauxite layers or lenses which, if they ever existed, have been removed by erosion.

The pocket deposits of bauxite generally show sharp contacts with the enclosing limestone or clay, although some deposits in clay show gradational margins of bauxitic clay high in alumina. Similarly, bauxite pockets in limestone may be directly in contact with the limestone or may be separated from it by masses of residual earth, such as terra rossa, derived from limestone decay. The shape of the pockets is irregular; some are approximately equidimensional but most are irregularly pod-shaped. The manner in which they cut across the bedding of the enclosing rocks, and their arrangement in groups, suggests deposition of the protore as fillings of solution caverns.

*Detrital Deposits.*—Detrital bauxite deposits originate from other pre-existing bauxite deposits, and may be talus accumulations, stream gravels or sands, or more or less consolidated low-level surface layers.

#### ORIGIN

The hypotheses that have been advanced to explain the origin of bauxite may be grouped under three main headings: (1) chemical sedimentation, (2) weathering *in situ*, (3) detrital deposition.

Many geologists have considered it necessary to explain the formation of bauxite deposits by processes of solution and redeposition. Clays or other aluminum-bearing rocks were looked upon as the source of the aluminum. As solvents, various acids and alkalies were taken into consideration—for instance, nitric acid, derived from bacterial activity, or from lightning discharges; sulphuric acid resulting from the decomposition of sulphides and sodium hydroxide or sodium carbonate, obtained by decomposition of various rocks.

In recent years the role of weathering processes in the formation of bauxite and laterite has been clearly recognized, and the general opinion today is that most bauxite deposits, rather than being the result of solution and redeposition of aluminum, are residual products resulting from the intensive weathering of aluminum-bearing rocks, involving the solution and removal of constituents other than aluminum. This process is called lateritization, and the original rocks most commonly involved are syenite, granite, basalt, diabase, crystalline schists, limestone, shale and clay. It is evident, therefore, that the bauxite itself may be somewhat younger geologically than the bedrock with which it is associated.

Certain bauxite deposits of minor importance are believed to be of detrital origin, being the result of mechanical concentration of bauxite fragments from previously existing bauxitic materials and in places their partial consolidation by infiltration of cementing substances.

#### DISTRIBUTION OF DEPOSITS

Although bauxite deposits occur abundantly in many parts of the world, the mining of bauxite in important quantities is confined to relatively few countries. Roughly, in the order of their importance, the principal bauxite-producing countries, not including Russia, are France, United States, Dutch Guiana, British Guiana, Hungary, Italy and Yugoslavia. Russia has entered the ranks of important producers only within the last three or four years. Minor quantities of bauxite are produced in Greece, northern Ireland, India, Rumania, Spain, Australia and Germany. France produces roughly one-third of the world's bauxite, the United States approximately one-fifth, Dutch Guiana, Hungary and British Guiana, each about one-tenth, Italy about one-fifteenth, and Yugoslavia about one-twentieth (Fig. 1).

*France.*—The principal bauxite deposits of France occur in the departments of Var and Herault; minor deposits in the departments of Bouches de Rhone and Ariege. About four-fifths of the bauxite produced in France has come from the Var district, and three-quarters of the remainder from Herault. Besides furnishing the total requirements of France, these deposits have supplied a considerable portion of the bauxite used elsewhere in Europe, particularly in the United Kingdom and Germany. Bauxite was discovered in France in 1821, near Les Baux in Bouches du Rhone, from which locality it receives its name. The first recorded production occurred there in 1873.

The French bauxite is mostly of the dark red, high-iron type. This variety ordinarily contains 56 to 59 per cent  $\text{Al}_2\text{O}_3$ , 20 to 25 per cent  $\text{Fe}_2\text{O}_3$ , and 2 to 5 per cent  $\text{SiO}_2$ . Small amounts of white and gray bauxite are produced, the former containing 60 to 70 per cent  $\text{Al}_2\text{O}_3$ , about 4 to 12 per cent  $\text{Fe}_2\text{O}_3$ , and 8 to 16 per cent  $\text{SiO}_2$ , and the latter having a variable composition ranging between the red and the white bauxite. All

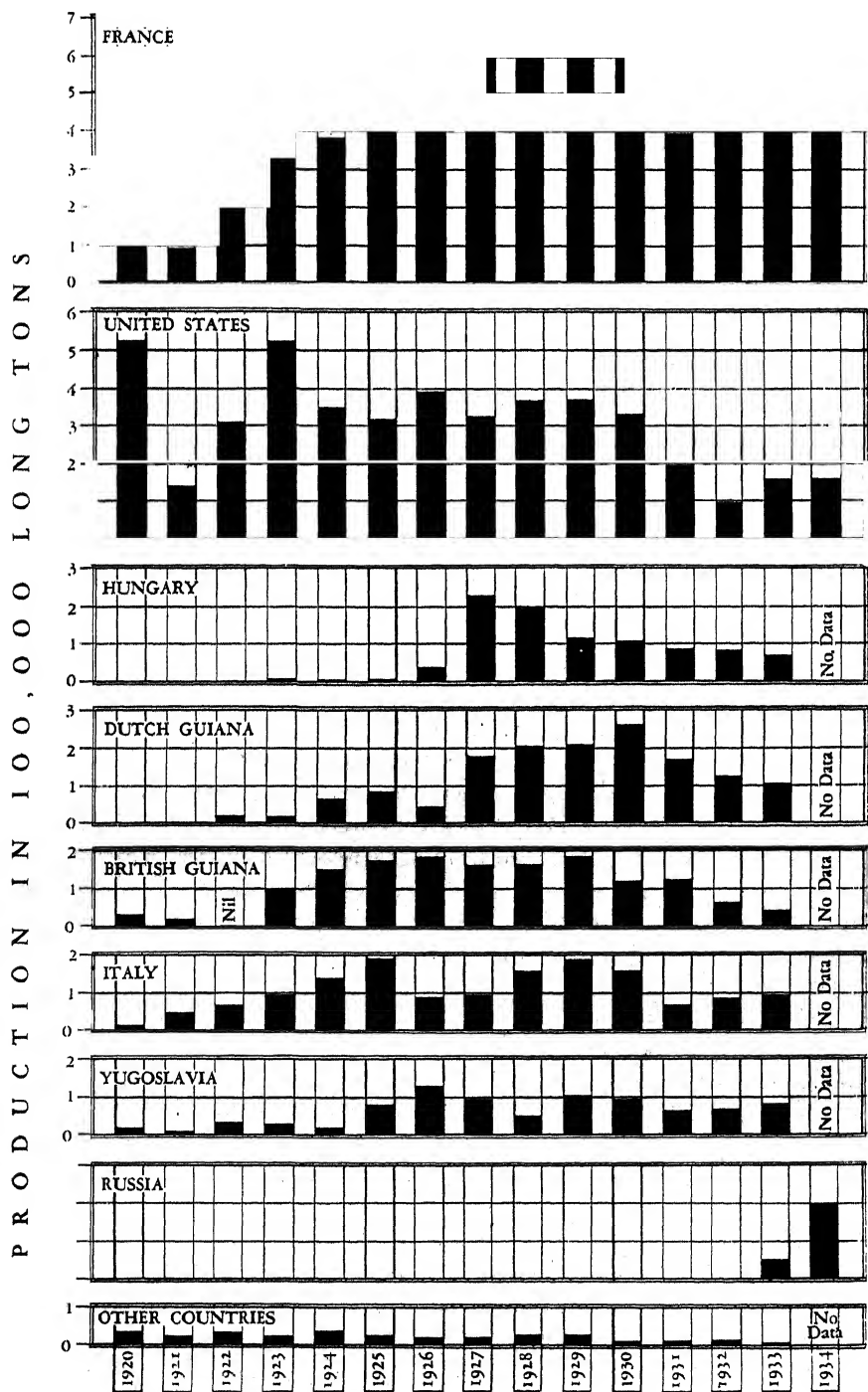


FIG. 1.—BAUXITE PRODUCTION BY COUNTRIES, 1920 TO 1934.

three types contain 12 to 14 per cent combined water. The different varieties all occur in association with limestone as pockets or interlayered beds and lenses. They vary in relative abundance in the different districts.

*United States.*—Bauxite was first discovered in the United States near Rome, Ga., in 1883. The first production occurred in Georgia in 1889 and in Arkansas 10 years later. Deposits occur in Arkansas, Georgia, Alabama, Tennessee and Mississippi. The Arkansas deposits have furnished about 90 per cent of all the bauxite produced in the United States. They are alterations of nepheline syenite and clay and are overlain by Eocene clays. The deposits in northern Georgia, northern Alabama and Tennessee occur as pockets in clays; those in southern Georgia and southern Alabama are in the form of beds and lenses interlayered in Eocene sediments.

The bauxites of the United States differ from those occurring in Europe in that usually they contain a relatively small amount of iron oxide and carry a high content of combined water. On an average they contain 56 to 59 per cent  $\text{Al}_2\text{O}_3$ , from less than 2 to about 6 per cent  $\text{Fe}_2\text{O}_3$ , from 5 to 8 per cent  $\text{SiO}_2$  and approximately 29 to 31 per cent combined water. In general the deposits in Georgia, Alabama and Tennessee are lower in iron oxide and higher in silica than those in Arkansas. The bauxite deposits of Mississippi are of low grade and under present conditions are considered uncommercial.

There occur also in the United States, in central Missouri, numerous but small and scattered deposits of diaspore, which have furnished an important production in recent years, being used mainly in the manufacture of aluminous refractories. The Missouri diaspore, which forms small irregular masses in flint-clay pockets, varies in alumina content from 50 to more than 70 per cent, depending on the amount of intermixed clayey materials. The low-grade diaspore is known as burley clay.

*Dutch Guiana.*—Bauxite was discovered in Dutch Guiana about 1915 and the first shipments were made in 1922. Most of the ore is exported to the United States for manufacture of aluminum. It is found along Surinam, Cottica and Coermotibo Rivers, south and southeast of Paramaribo, and about 15 to 25 miles inland from the coast. It is of the tropical lateritic variety and occurs mostly as surface deposits, forming low hills and ridges in the coastal lowlands, with only a few feet of soil overburden. The Dutch Guiana bauxite is of high grade, containing 57 to 59 per cent  $\text{Al}_2\text{O}_3$ , 5 to 7 per cent  $\text{Fe}_2\text{O}_3$ , 1.5 per cent to 2.5 per cent  $\text{SiO}_2$  and 31 to 32 per cent combined water.

*Hungary.*—The Hungarian bauxite deposits occur in an area north of Lake Balaton and extend thence northeastward toward Budapest. Most of the ore produced thus far has come from the Vertes Mountains, in the northeastern part of the belt. The bauxite ranges from yellow to brown and red in color, and that of commercial grade contains 57 to 60 per

cent  $\text{Al}_2\text{O}_3$ , 12 to 20 per cent  $\text{Fe}_2\text{O}_3$ , 2 to 7 per cent  $\text{SiO}_2$  and 14 to 16 per cent combined water. However, a large proportion of the material in the deposits is of low grade and must be removed along with the commercial ore, increasing the mining expense. The Hungarian bauxite is similar to that of the Mediterranean region in being associated with limestone in pockets and lenses. It was first exploited in 1925 and since that time has furnished a large proportion of the bauxite used in Europe for aluminum manufacture.

*British Guiana.*—Bauxite was first exploited in British Guiana in 1914 and shipments began in 1917. The principal deposits are in the Demerara and Berbice River regions, from 65 to 125 miles south and southeast of Georgetown. They occur as horizontal or slightly tilted beds and lenses, in places outcropping along the rivers and small creeks and elsewhere overlain by a varying thickness of recent coastal deposits. In the exploited areas this overburden of sand and clay ranges up to 100 ft. or more in thickness and overlies 15 to 25 ft. of bauxite. British Guiana bauxite contains 59 to 61 per cent  $\text{Al}_2\text{O}_3$ , 1 to 2.5 per cent  $\text{Fe}_2\text{O}_3$ , 2.5 to 4 per cent  $\text{SiO}_2$  and 30 to 32 per cent combined water. It is used mainly for manufacture of aluminum but because of its low content of iron oxide it is also in great demand for the manufacture of chemicals and refractories. Most of it is exported to Canada and the United States but considerable tonnages are shipped also to the United Kingdom and continental Europe.

*Italy.*—Important deposits of bauxite occur in the Istrian Peninsula south and southeast of Trieste. Most of them are in the form of pockets in limestone, abundant and widely scattered. The mining of bauxite in Istria on an important scale began during the World War and these deposits have since furnished not only the Italian requirements but important tonnages annually for export to other European bauxite-consuming countries. Large but relatively low-grade bauxite deposits occur in the central Apennine region of Italy and periodically have furnished a small production.

The Istrian bauxite is of two main types; one, dark red, similar to that produced in southern France and the other a yellowish variegated ore. The former generally contains between 55 and 58 per cent  $\text{Al}_2\text{O}_3$ , 22 to 25 per cent  $\text{Fe}_2\text{O}_3$ , 2 to 4 per cent  $\text{SiO}_2$  and 12 to 14 per cent combined water. The latter commonly carries 60 to 65 per cent  $\text{Al}_2\text{O}_3$ , 10 to 15 per cent  $\text{Fe}_2\text{O}_3$ , 5 to 9 per cent  $\text{SiO}_2$  and 12 to 14 per cent combined water. The different varieties may occur together in the same deposit or they may form separate deposits.

*Yugoslavia.*—The Yugoslavian bauxite deposits occur mainly in the provinces of Dalmatia, Herzegovina and Montenegro. Only those of Dalmatia have been extensively exploited, as the Herzegovinian deposits have been opened up only within the last year, while the Montenegrin deposits are mostly of low grade. Most of the bauxite mined in Dalmatia has come from Drnis district, about 50 miles north-

east of Sibenik, but there are also mines in the Obrovac district and on some of the coastal islands. The Yugoslavian bauxite is of the dark red variety common elsewhere in southern Europe but differing from other European bauxite in that it contains a higher percentage of combined water. It contains approximately 50 to 54 per cent  $\text{Al}_2\text{O}_3$ , 20 to 24 per cent  $\text{Fe}_2\text{O}_3$ , 1 to 3 per cent  $\text{SiO}_2$  and 18 to 22 per cent combined water. Bauxite mining began in Yugoslavia during the World War, and much of the bauxite used by the Central Powers during this period was obtained from this source.

*Russia.*—Since the beginning of the first Five-Year Plan, Russia has come to the front as a producer of bauxite. The bauxite mined thus far has been derived from the Tikhvinsk district southeast of Leningrad, but during the last few years there have been reports of important bauxite discoveries in the Ural Mountains north and south of Sverdlovsk. The Tikhvinsk bauxite contains about 35 to 54 per cent  $\text{Al}_2\text{O}_3$ , 15 to 20 per cent  $\text{Fe}_2\text{O}_3$ , 10 to 20 per cent  $\text{SiO}_2$  and 10 to 20 per cent combined water. The ore produced at present is being used mainly in the manufacture of aluminum at the new Russian smelting plants at Volkhov and on the Dnieper River. It is of very low grade, however, and would be considered uncommercial except from the nationalistic viewpoint.

*Greece.*—Although not as yet a large producer of bauxite, Greece contains important deposits, some of which are in process of development at the present time. The principal Greek bauxite occurs in the region north of the Gulf of Corinth, but deposits are also found in Euboea and on certain islands in the Aegean. On account of their proximity to the coast, they are well situated for exploitation. The Greek bauxite, although of the dark red ferruginous type, common in Europe, is harder and more refractory. It contains about 56 to 59 per cent  $\text{Al}_2\text{O}_3$ , 16 to 20 per cent  $\text{Fe}_2\text{O}_3$ , 3 to 7 per cent  $\text{SiO}_2$  and 13 to 15 per cent combined water.

*Netherlands Indies.*—The bauxite deposits of the island of Bintan, near Singapore, have been developed within the last three years to supply the new Japanese aluminum industry. Some ore has recently been shipped to Germany, analyzing approximately 55 per cent  $\text{Al}_2\text{O}_3$ , 2.50 per cent  $\text{SiO}_2$ , 15 per cent  $\text{Fe}_2\text{O}_3$  and 29 per cent combined water.

*Other Countries.*—The bauxite deposits of Rumania are similar to those of Greece. Because of their remoteness from markets, they are not being exploited. The bauxite of British India is of two types, that occurring in the Central Provinces and in southern and southeastern India, which is of the ordinary, lateritic type, and that of the Jammu district, Kashmir, in northwestern India, which is of the diaspore type. Indian bauxite is being shipped in small amounts to Japan and Europe. The bauxite of northern Ireland is a low-grade clayey type, locally high in iron oxide. Small and relatively unimportant bauxite deposits have been exploited in Spain, Germany and Australia.



Large and numerous deposits of bauxite occur in various tropical and subtropical countries but have remained undeveloped mainly because of their remoteness from bauxite-consuming centers. Such are the deposits of French Guinea, Gold Coast and elsewhere in West Africa, those of Nyasaland in East Africa, and of Minas Geraes, Brazil.

#### POLITICAL AND COMMERCIAL CONTROL

Like most mineral raw materials, bauxite supplies are unequally distributed among the important world powers, particularly from the viewpoint of the aluminum industry in these powers.

The United States, as the leading producer in the world of metallic aluminum, aluminum chemicals and aluminous abrasives, is insufficiently supplied with bauxite reserves. Although the United States deposits furnish an important production, a large tonnage of bauxite is annually imported and little is exported, except in the form of refined products. In spite of this situation, there is an import duty of \$1 per ton on bauxite brought into the United States.

Germany, as the next largest producer of metallic aluminum and aluminum products, has practically no commercial bauxite within its borders. The German bauxite requirements are obtained mainly from Hungary, and subordinately from France, Italy and Yugoslavia. About a year ago a substantial import movement began from the Netherlands Indies. France and Italy, during the last year or two, have placed restrictions on the exportation of bauxite, making it increasingly difficult for Germany to obtain supplies from these sources.

France is well supplied with bauxite reserves and may rely on its own deposits to furnish the requirements of the domestic aluminum and other bauxite-consuming industries for many years to come. France imports no bauxite from abroad, but has exported substantial quantities to United Kingdom, Germany and elsewhere.

Although there are no bauxite deposits in the United Kingdom itself, the British Empire is well supplied with bauxite, both developed and undeveloped. Of these, among the most important are those in British Guiana, which supply the Canadian aluminum industry, and are furnishing increasing quantities to the United Kingdom. Other important, but as yet largely undeveloped, deposits occur in British India, Gold Coast Nyassaland. Most of the bauxite requirements of the United Kingdom have in the past been imported from southern Europe, chiefly from France. It may be expected, however, that with the present tendency towards economic nationalism these sources will become more restricted and the United Kingdom will have to depend increasingly upon the bauxite resources of the British Empire.

Norway and Sweden, with their important aluminum industries, are dependent entirely upon imported bauxite. In the past bauxite supplies

have been obtained mainly from France and Italy, but it is conceivable that in the not far distant future Scandinavian aluminum producers will have to go farther afield for their bauxite requirements.

Switzerland, an important producer of aluminum, has no bauxite deposits. Raw materials for its plants have been obtained largely from France in the form of alumina manufactured from French bauxite.

Italy has substantial bauxite reserves, which will be able to supply the domestic aluminum and other bauxite-consuming industries for some time in the future.

Hungary produces aluminous cement and also a small amount of aluminum in a recently built plant. A relatively minor part of its bauxite output, however, is used internally.

Russia, with its rapidly expanding aluminum industry, has a dearth of aluminous raw materials. The presently developed bauxite deposits, although uneconomical, will serve to supply the domestic consuming industries for a brief period, but it is clear that the time is approaching when Russia will find it necessary to go across its borders for bauxite supplies if its alumina and aluminum plants are to be kept operating.

Japan has ambitions to become independent with regard to its aluminum requirements. However, Japan has no bauxite deposits and it is not likely that large deposits will be discovered in territories under its control. Until recently the small aluminum-producing plants in Japan were using Korean alunite and Manchurian clays. Small amounts of European and British Indian bauxite have been imported and bauxite deposits in the Netherlands Indies have been developed, looking to a future Japanese market. An important movement from this latter source to the new Formosa smelter has already begun.

A number of countries possess important bauxite deposits but have no aluminum or other important bauxite-consuming industries. Thus the Netherlands has large bauxite deposits in Dutch Guiana and in the Netherlands Indies, the former furnishing an important part of the United States requirements and the latter, as already mentioned, being developed for the expanding Japanese industry. Yugoslavia has exported important tonnages of bauxite annually to Germany and elsewhere, but has consumed very little within its own borders. Brazil also has large bauxite deposits but has negligible bauxite-consuming industries.

#### PRODUCTION AND CONSUMPTION

Although bauxite was discovered in France in 1821 there is no record of any production until 1873, when 200 tons was mined. At the end of the century the output had not reached 50,000 tons. Thereafter, however, bauxite mining progressed rapidly and in 1913 more than 300,000 tons was produced. In the United States the first bauxite production dates from 1889, when 728 tons was mined in the Rome district. The Arkansas bauxite mines began producing in 1899, with an output of 5045 tons in

that year. Until the World War started, more than 95 per cent of the bauxite produced annually came from the mines of France and the United States. During the war, however, the necessity for the opening up of new bauxite deposits became apparent and while the deposits of Istria and Dalmatia were being developed by the Central Powers, the Allies turned their attention to the newly discovered deposits of British and Dutch Guiana. British Guiana mines started shipments in 1917 and the Dutch Guiana mines in 1922. Somewhat later bauxite was discovered in Hungary and was developed for the benefit of the German aluminum plants. A very recent entrant into the ranks of producers is Russia, with a spectacular rise in production in 1933 and 1934.

### PROSPECTING, EXPLORATION AND MINING

*Prospecting.*—Although bauxite deposits were formed under conditions existing in warm climates, they are not necessarily confined to tropical or subtropical regions, owing to variations in climatic conditions in past geologic times. Thus the Arkansas bauxite deposits occur at latitude 35° N., those of southern Europe between 40° and 50° N. and those of the Tikhvinsk region in Russia at latitude 60° N. Bauxite deposits are usually discovered from outcrops and fragments of float. Rock associations, however, may serve as a guide, bauxite being commonly found with clay, limestone or certain igneous rocks, such as syenites, feldspathic schists and basalts. Probably the most striking association of bauxite is with old land surfaces. Thus bauxite deposits in the older rocks occur along unconformities representing long time intervals, while those of recent origin occur on moderately level, peneplained surfaces that have been undisturbed for a long period of time.

*Exploration.*—Once found by outcrops, bauxite deposits are explored by drilling. It is generally preferable to use hand drills, as most bauxite deposits occur in remote regions where transportation is difficult. Moreover, many bauxite deposits are found at relatively shallow depths and power drills are unnecessary. Core drills usually are not suitable, as bauxite and the associated sediments are relatively soft and do not yield satisfactory cores. It is best to perform the exploration by drills in two stages, the early drilling, widely spaced, and merely for the purpose of determining the quality and estimating approximate tonnages, and the later drilling at close intervals to serve as a guide to mining. A few test pits should be sunk on all deposits to supplement the drilling, mainly with the object of securing samples for washing and other beneficiating tests.

*Mining Methods.*—The methods used in mining bauxite differ somewhat in different countries and with different types of deposits. In deposits occurring in the form of extensive surface blankets or in beds and lenses interlayered with unconsolidated sediments, such as are being mined in Arkansas and in northern South America, quarrying is a common method of mining. The overburden, where present, is removed by

hand or by scrapers or, where thick, by power shovels or draglines, and the upper surface of the bauxite layer is thoroughly cleaned by means of picks and shovels. Holes for blasting are then drilled into the bauxite bed vertically, starting at the surface and penetrating into the lower portion of the bauxite layer. Generally such holes are drilled in series parallel to the existing quarry faces. After blasting, the broken bauxite is picked up by power shovels, loaded on mine cars and transported by rail to beneficiation plants.

Where the overburden is too deep to be removed by stripping, or where lenses and layers of bauxite are interlayered with solid rock, such as limestone in the European fields, and the attitude of the enclosing rock is such that the deposits reach considerable depths, quarrying methods are used only along the outcrops and underground mining is resorted to at depths. The underground mining is advanced by a series of drifts and crosscuts and caving is employed in retreating. The bauxite is removed from the workings in mine cars, through tunnels, shafts or inclined planes, according to the form of the deposit and the method of working, and is transported from the mines to railway stations or seaports by motor lorries. European bauxite is not subjected to beneficiation.

Pocket deposits of bauxite, such as occur enclosed in limestone at various places in southern Europe and in clay in southeastern United States, are mined by open quarrying methods. Bauxite pockets are usually of limited extent and the mining is mainly by hand with the use of picks, shovels and wheelbarrows. In large pockets mine cars may be used. The bauxite is raised from the open pits along inclines or by elevators, and transported to railway stations by motor lorries. At several localities in Europe where the conditions permit, aerial cableways are in use between mines and loading stations.

#### PREPARATION FOR MARKET, TESTS AND SPECIFICATIONS

*Preparation.*—In Arkansas, British Guiana and Dutch Guiana the bauxite is beneficiated before marketing. In Europe the bauxite is shipped direct to consuming plants in the crude state as mined. In the United States and in the Guianas the crude bauxite, as mined, consists of fines and fragments ranging in size up to a foot or more and contains 12 to 15 per cent free moisture. This crude bauxite is crushed to a maximum size of  $2\frac{1}{2}$  to 3 in. and is then washed to remove the clay and other impurities present. The washing is generally performed in trommel-rake washers but locally vibrating screens are used to supplement these.

As the washed bauxite contains about 15 to 18 per cent moisture, it is dried before shipment, in rotary kilns that remove all except 1 to 3 per cent of the free moisture. The rotary kilns range from 60 to 120 ft. in length and 6 to 8 ft. in diameter, depending upon the size of the operation.

They are lined with firebrick. The temperature of the bauxite leaving these kilns is about 200° F. and 35 to 40 tons per kiln hour may be produced. This is the ordinary crushed, washed and dried bauxite consisting of mixed lumps and fines that is marketed for the manufacture of aluminum and for chemical, abrasive and refractory purposes. The main reason for drying the bauxite at the mines is to save transportation costs, but drying is also important for the fabricating plants where the bauxite is to be consumed, as the fine grinding necessary for further treatment during processing requires a dry material.

It is desirable, when bauxite is used for abrasive and refractory manufacture, that the combined water as well as the free moisture should be removed. Therefore some bauxite producers are equipped with rotary kilns designed especially for calcining. Such kilns range up to 150 ft. or more in length and have heavy refractory linings. The calcining process yields only about 3 to 4 tons of bauxite an hour. The calcined mineral leaves the kiln at a temperature of 1700° to 1800° F.

*Tests and Specifications.*—The bauxite to be used in the various consuming industries differs considerably in composition. To be suitable for the manufacture of metallic aluminum and aluminous abrasives, bauxite should be as low as possible in silica. Preferably, it should contain less than 2.5 or 3 per cent  $\text{SiO}_2$ . The iron oxide content is immaterial and may be as high as 20 to 25 per cent. When used in the manufacture of aluminous chemicals and refractories it is important that the bauxite should contain as little iron oxide as possible. Bauxite for aluminum sulphate manufacture should contain a maximum of 2 per cent  $\text{Fe}_2\text{O}_3$ . Bauxite for the manufacture of refractories should preferably not contain more than 1.50 per cent  $\text{Fe}_2\text{O}_3$ . For all purposes it is important that the alumina content should be as high as possible, consistent with the price.

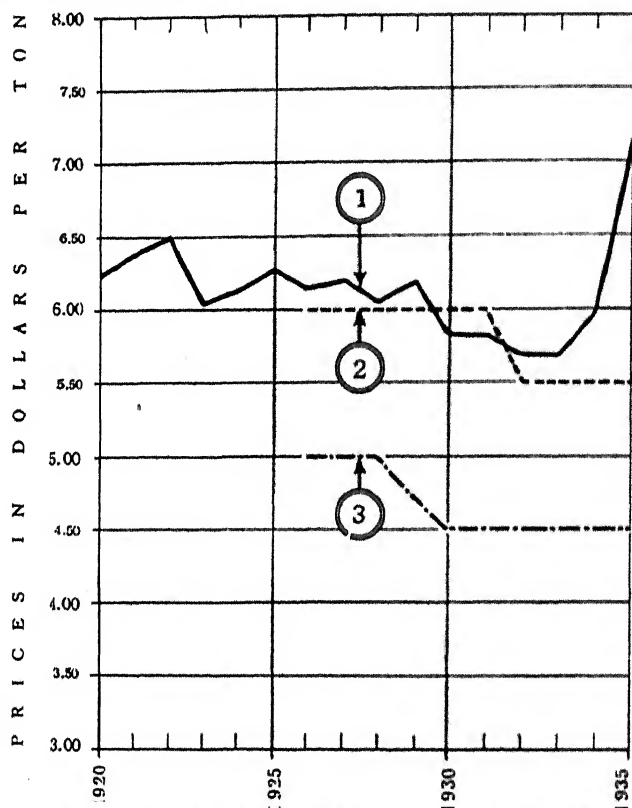
#### MARKETING, USES AND PRICES

*Marketing and Uses.*—As indicated, the main uses of bauxite are in the manufacture of metallic aluminum and aluminous chemicals, aluminous abrasives and aluminous refractories. In a minor way bauxite is used in the manufacture of aluminous cement, in oil filtration and in the smelting of iron. In the manufacture of metallic aluminum the bauxite is first purified by chemical methods, the resultant product, aluminum hydrate, being calcined to produce alumina. The alumina is smelted to metallic aluminum in electrolytic baths consisting essentially of molten cryolite.

The principal aluminous chemicals produced from bauxite are aluminum sulphate, aluminum hydrate, aluminum chloride and sodium aluminate. Aluminum sulphate is produced by treatment of bauxite with sulphuric acid. Aluminum hydrate and sodium aluminate result from treatment of bauxite with caustic soda. Aluminum chloride is produced by treating heated bauxite with chlorine gas.

Aluminous abrasives are produced by melting bauxite or alumina in small electric furnaces. After solidification and crystallization of this molten product, it is crushed and ground, and constitutes the crude abrasive from which grinding wheels, oilstones, abrasive cloths and papers, abrasive powders and other commercial abrasive products are manufactured.

Aluminous refractories are produced from ground bauxite or alumina by mixing them with a binder, pressing into forms and putting through a baking process. Aluminous refractories, although somewhat more



1. Average annual price per long ton of domestic bauxite, f.o.b. mines, U.S.A.
2. Average quoted price of French bauxite per metric ton, c.i.f. U.S. Atlantic ports.
3. Average quoted price of Dalmatian bauxite per metric ton, c.i.f. U.S. Atlantic ports.

FIG. 2.—BAUXITE PRICES, 1920 TO 1935.

expensive than ordinary fire-clay refractories, are much more resistant to heat, abrasion, corrosion, spalling and erosion, and therefore are being increasingly used where severe furnace conditions are encountered. Fused aluminous refractories of the mullite type are commonly cast directly from the melt.

Aluminous cement is characterized by its rapid-hardening qualities and resistance to chemical action and heat. Aluminous cement is said

to reach the same degree of hardness and strength in 24 hr. that is reached by ordinary Portland cement in 28 days. However, there are certain super-Portland cements that harden in four or five days, and this has militated against the more extensive use of aluminous cement for general purposes.

Bauxite is said to be effective in desulphurizing, deodorizing and decolorizing oils and other liquids. It is being commercially used for this purpose in the filtering of kerosene. Other uses involving filtration are in prospect. Bauxite is used also in the smelting of iron as a slag corrective.

*Price.*—Fig. 2 shows the average price of domestic bauxite in the United States, as well as the average prices quoted for delivery at United States ports on Dalmatian and French bauxite.

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## BENTONITE

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**B**ENTONITES are clays that have been derived from volcanic ash and that have the clay mineral montmorillonite for their chief constituent. For many years the name was solely applied to a specific type of clay with unique characteristics, then known to occur only in the vicinity of the Black Hills of Wyoming and South Dakota. Recently, however, the term has been extended to cover a broad class of claylike materials that are petrographically similar<sup>3</sup> but that differ widely in physical properties from the original Black Hills type.

## CLASSES

The bleaching-earth types of clays are discussed in chapter VII, therefore this paper will deal only with the technical and utilitarian aspects of the Black Hills type of bentonite.

The broad family of bentonites may be divided into two general classes: (1) those that adsorb large quantities of water, "swelling" enormously in the process, and that have the property of remaining in suspension in thin water dispersions; (2) those that absorb practically no more water than ordinary plastic clays or fuller's earths, do not swell noticeably, and settle rapidly in thin water dispersions. There are, of course, some intermediate gradations.

Type 1 has a wide variety of commercial uses, because of properties that are unique in an inorganic material. Type 2 is produced in larger tonnages, practically all of the consumption being for clarifying and bleaching in the oil industry, and is analogous to fuller's earths and bleaching clays.

Deposits of the highly absorbent Black Hills type of bentonite, described as type 1, occur chiefly in eastern Wyoming and western South Dakota, overlapping into Montana and adjacent Canadian provinces. Western Wyoming has deposits nearly similar but with slightly less absorbent properties. California contains some of this type also, although the main production of California bentonite is of the bleaching-earth variety. Utah and Nevada have scattered deposits of intermediate gradations.

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<sup>3</sup> References are at the end of the paper.

The large bodies of bentonite in Texas, Arkansas, Mississippi, Kentucky and Tennessee are of the nonswelling, nonsuspendible type, as are also numerous smaller deposits in other states not mentioned here. The geological departments of some states group bentonite and fuller's earth together in their reports.

### PROPERTIES

The clay-mineral montmorillonite forms about 95 per cent of the substance of bentonite, with small fractions of feldspar, gypsum and calcite, and traces of quartz, volcanic glass, biotite and zeolites. When the raw material, without fine grinding, is dispersed in water, about 10 per cent of its particles will be larger than 10 microns in size, 15 to 20 per cent between 10 and 0.5 microns and the remainder immeasurably finer. The montmorillonite portion is in the shape of flat plates, of visible width and breadth under the ultramicroscope but of colloidal thickness, and this peculiar structure gives it a tremendous surface area.

Norton and Hodgdon,\* at the Massachusetts Institute of Technology, found some interesting facts in a series of experiments with seven finely powdered materials. Table 1 gives the computed average size of the grains of these materials down to 0.00003 cm., and the average surface area for one gram of particles.

TABLE 1

Material	Average Number of Grains per Linear Cm.	Average Area for One Gram of Material, Sq. Cm.
Dry-milled quartz. .	1,400	2,900
Wet-milled quartz. .	4,000	9,000
Calcined china clay.	1,100	2,400
China clay.....	2,400	5,510
Brick clay.....	2,600	5,800
English ball clay....	3,400	7,400
Bentonites <sup>a</sup> .....	20,000	50,000

<sup>a</sup> Estimated from rough microscopic observation.

To get some conception of the voids between the dry particles, i.e., the dry porosity, they made a series of tests subjecting a mass of each of the dried materials to three pressures—8, 80 and 800 kg. per sq. cm. (approximately 114, 1140 and 11,400 lb. per sq. in.). Bentonite was the only one to show practically no variation in porosity. To quote, "The minimum dried spacing (of the bentonite) is about the same for all

\*Norton and Hodgdon: Some Notes on the Nature of Clay. *Jnl. Amer. Ceram. Soc.* (1932) 15, No. 3.

pressures and the porosity reached is only 6 per cent. This would indicate a close packing of a platelike material." In these tests, the bulk volume of the mass of bentonite was not reduced even at the highest pressure used.

In a further series, the materials were wetted and subjected to pressures of 8 kg. per sq. cm., and a computation was made of the water film surrounding the particles, as shown in Table 2.

TABLE 2

MATERIAL	MAXIMUM THICKNESS OF WATER FILM, CM.
Dry-milled quartz.....	0
Wet-milled quartz.....	0
Calcined china clay.....	$0.1 \times 10^{-5}$
English china clay.....	$2.1 \times 10^{-5}$
Brick clay.....	$3.1 \times 10^{-5}$
English ball clay.....	$2.4 \times 10^{-5}$
Bentonite <sup>a</sup> .....	$3.3 \times 10^{-5}$

<sup>a</sup> Note that the bentonite has the thickest water film.

In another series the wetted masses were subjected to the same pressures applied to the dried masses. No matter what pressure was applied to the bentonite, a film of water of a certain thickness was always present and could not be squeezed out. To quote, "the thickness of the water film (on the bentonite) at any given water content cannot be reduced below a certain minimum with pressure at least up to 800 kg. per square centimeter."

A high-grade bentonite will absorb nearly five times its weight of water and at full saturation it increases in volume up to 15 times its dry bulk. With 6 to 7 parts water it becomes a gelatinous paste, the consistency of heavy grease. With 18 to 20 parts water it forms a thin sol in which the bentonite will remain in suspension indefinitely. Even in a concentration as low as one part bentonite to 5000 parts distilled water, 70 per cent of the bentonite will remain suspended for months.

The swelling property is reversible; it can be dried and re-swelled an infinite number of times and this activity is unaffected by temperatures below 450° F. However, the bentonite will not re-swell if in its first saturation cycle it is admixed with over 10 per cent of added alkali as Portland cement.

Its gels and sols increase in inherent consistency on standing, reaching their maximum in two or three days. In addition, they show pronounced thixotropic tendencies. The bentonite suspensoids are negatively charged, show Brownian movement, and are profoundly affected by electrolytes in the water. Dispersions of natural bentonite have an average pH of about 9.2, which is also their isoelectric point.

Three factors cause bentonite to swell in water: (1) water penetrates the crystal lattice of the mineral (no other crystal has this property, so far

as known) expanding the lattice by capillary pressure;\* (2) water forms a stable film around each particle, pushing them apart; (3) the particles mutually repulse each other because of like negative polarity.

Actually, the "swelling" is a diffusion of bentonite particles through the water; they take up more space in water than in air because they become bulkier as their crystal structure expands and because the individual envelopes of water move with the particles. Thus the volume of "free" water is reduced and the mass assumes a viscous consistency. The total volume of this mass, however, will be no greater than the sum of the original bentonite and water volumes.

### ORIGIN

The Black Hills bentonites were deposited originally as volcanic dust, which settled in the salt seas that covered the Northwest. The region alternated between land and sea and the glassy particles—of which traces are still found in the present bentonite—were gradually divitrified by chemical decomposition and hydration. The seepage of salt and alkaline waters and the dissolving of fragments of other minerals slowly altered it to the gel-forming bentonite of today.

### MINING AND PRODUCTION

The chief region of commercial production is in Wyoming and South Dakota, in a horseshoe-shaped area lying north and west of the Black Hills. A small quantity of a related but not exactly similar kind is produced in California and a very small amount in British Columbia.

The commercially workable Black Hills deposits are from 2 to 4 ft. thick, close to the surface, and contain 25 to 45 per cent moisture. Overburden from a few feet up to 10 ft. is removed, and the bentonite is dug and hauled by trucks to the processing plants, which sometimes are 10 to 15 miles away. It is dried in rotary driers down to 8 per cent moisture, then granulated or powdered for shipment. The usual commercial grade is in the form of a powder 90 to 95 per cent minus 200-mesh by dry sieve test, and is packed in 100-lb. bags.

While there was some consumption of bentonite as early as 1888, it was mainly experimental and actual production was irregular and in small quantities up to 15 years ago. In 1925 shipments were about 2500 tons from two plants and in 1935 were 42,000 tons from six producing plants in Wyoming and South Dakota.

\* German scientists\* report the swelling of the crystal structure of bentonite as follows:

PERCENTAGE OF WATER  
IN BENTONITE

8.7

23

30

SWELLING, Å.

11.2

15.2

19.6

## USES

More than half the Black Hills type of bentonite produced is used in metal foundries as an ingredient of molding sands. It has bonding properties far greater than other clays, so that less clay is required in the sand, thus allowing more free space between the sand grains for rapid egress of the steam and gases created during the pouring of the metal. It also permits the sand to be worked with lower moisture, thus making less steam.

In sinking oil wells bentonite is used for thickening the drilling mud so that it will suspend rock cuttings and carry mud-weighting materials; also because of its property of sealing the walls of the well against water filtration. A new and growing use is for stopping water flow or leakage in engineering works. A thin blanket of bentonite placed on the outside of a subsurface building wall or floor or between forms, as in mine seals, trenches or cofferdams, will effectually stop the percolation of water. A slurry of bentonite pumped under pressure into subsurface sand, gravel or seamy rock strata, as under dams, reservoirs, etc., will seal the voids against water passage.

Bentonite performs detergent functions, owing to a combination of colloidal activity and high absorption (particularly for carbonaceous soil) and hence a considerable volume is consumed in laundries, especially for washing heavily soiled articles. It is used as an additive plasticizing and bonding agent in combination with other clays and ceramic materials to improve burned clay products. Many heat and sound-insulating blocks, plasters and cements employ bentonite for their bonding medium. It is a standard suspending, spreading and adhesive agent in horticultural sprays and insecticides. A recent development is the use of bentonite for clarifying turbid waters and purifying sewage.

Other established uses are: for emulsifying asphalts and other water immiscibles; as an admixture in concrete to improve workability and flow and to prevent segregation; to inhibit the gumming of screens in dewatering paper pulp; to gelatinize wet-mash poultry foods; for clarifying wines; in cosmetics and pharmaceuticals; as a suspending, thickening and paste-forming agent in a wide variety of products and processes.

## PRICES

Powdered bentonite in bags, in carload quantities f.o.b. Black Hills producing plants, sold at \$30 per ton and upwards from 1923 to 1927. In 1928 and 1929 it ranged from \$25 to \$17 per ton and has since steadily declined, selling for \$11 and \$13 per ton in 1936. In dried, coarsely crushed form, shipped in carloads in bulk, the price in 1936 was \$7 to \$8 per ton.

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## BLEACHING CLAY

BY J. W. BELL\* AND S. R. FUNSTEN†

**T**HE term "bleaching clay" as used in the oil industries refers to clays that in their natural state, or after chemical activation, have capacity for adsorbing coloring matter from oil. Bleaching clays are frequently classified into two groups—those naturally active and those active after artificial activation with acid. Actually no sharp line can be drawn in this classification, since some varieties of naturally active clays can be made more active by artificial activation. Other naturally active clays are not appreciably affected by acid-treatment. Commercial chemically activated clays are generally several times more efficient than the best quality of natural commercial clays.

Fuller's earths fall within the general group of bleaching clays, and the commercial term "fuller's earth" has gradually grown to apply to natural clays, for the most part originating in southeastern United States (principally Georgia and Florida), susceptible of manufacture into granular grades for percolation. Earths of this type have not responded satisfactorily to acid activation. Fuller's earths are prepared in pulverized as well as granular form, therefore are adaptable to both the contacting and percolation processes.

The clays falling within the activable group are generally of bentonitic origin and are especially prevalent in southwestern United States. Because of the difficulties in obtaining a satisfactory granular product, these clays are prepared commercially only in the pulverized grade.

For the most part, bleaching clay is used commercially for refining oil. It is applied either by the percolation method or by the contacting method. Percolation refers to the passage of oil through a bed of granular clay, while contacting refers to direct agitation of oil and pulverized clay. In either case the refining action is obtained by intimate contacting of liquid and solid adsorbent.

## COMPOSITION AND PROPERTIES

*Composition.*—The raw clays from which bleaching earths are prepared are composed of hydrous aluminum silicates containing varying quantities of magnesium, iron, calcium and other substances. Chemical

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composition is not a reliable means of discrimination between nonactive, active and activable clays, therefore it has not been possible to forecast the quality of any clay on the basis of the analysis alone. Careful research on some thousands of deposits of activable clay with similar analyses produced only a relatively small number of high enough quality for commercial use. Table 1 gives typical analyses of representative clays of the foregoing classifications.

TABLE 1.—*Typical Analyses*

Analyses Computed on Percentage by Weight	Nonactive Clays			Active Clays		Activable Clays	
	Siliceous Fire Clay	Florida Kaolin	High- dium Clay	Commercial Fuller's Earth		Arizona Bentonite	
				Georgia	Florida	Activable	Activated
SiO <sub>2</sub> .....	72.05	45.67	71.35	53.42	52.92	50.08	55.70
Al <sub>2</sub> O <sub>3</sub> .....	17.21	38.45	11.45	10.06	9.42	15.00	13.13
Fe <sub>2</sub> O <sub>3</sub> .....	1.25	0.75	6.93	3.58	3.65	2.92	2.44
TiO <sub>2</sub> .....		0.10	0.47	0.52	1.18	0.84	0.33
CaO.....	0.45		1.79	1.29	1.91	2.60	0.31
MgO.....	0.75	0.05	2.00	9.18	9.08	4.54	3.46
K <sub>2</sub> O.....		0.06	0.24	0.64	0.98	0.12	0.13
Na <sub>2</sub> O.....			0.13	0.02	0.03	0.08	0.12
Cl.....			None	0.03	0.02	0.01	0.01
P <sub>2</sub> O <sub>5</sub> .....			0.57	0.12	1.21	0.02	0.05
SO <sub>3</sub> .....			None	0.02	0.04	0.04	0.72
CO <sub>2</sub> .....			Tr.	0.65	0.11	0.02	0.01
Ignition loss.....	8.56			9.42	10.19	8.29	7.48
Uncombined water...		14.86	5.30	11.83	9.06	15.63	15.77
Totals.....	100.27	9.94	100.23	100.18	99.79	100.14	99.65

*Properties.*—Properties of bleaching earths from different parts of the country or even in different parts of one deposit frequently vary over a considerable range, therefore it is necessary to generalize in discussing this subject. The fuller's earth type of clay is characterized by a lack of plasticity, large water content, foliated structure, and tendency, when water is removed from the clay, to adhere strongly to the tongue. Activable and bentonitic clays differ from fuller's earth in that they are characterized in general by waxy appearance and slaking or disintegrating rapidly in water; also, activable clays do not stick to the tongue as readily as fuller's earths. The best grades of bleaching earths are light gray or brown in color in the raw, wet state and nearly white after drying. However, some earths with colors ranging from brown to buff, cream and blue are of excellent quality. Activable bentonites slake but do not swell in water as much as the almost inactivable Wyoming bentonites.



Activable clays as a rule are heavier and denser than clays such as fuller's earth. A cubic foot of dried, ground fuller's earth weighs only a little more than half as much as the same volume of dried, ground Arizona activable earth or some naturally active earths in Texas.

Bleaching earth generally occurs in clearly defined horizontal strata. The naturally active clays generally reach a thickness of 8 ft., and frequently greater than that. Clays of the activable type rarely exceed 3 to 4 ft. in thickness of strata. The clay strata of good deposits are seldom contaminated by limestone or sand.

There have been numerous publications regarding geology and mode of occurrence of bleaching earths; among them papers by Nutting,<sup>27</sup> Ross and Kerr,<sup>14</sup> T. W. Vaughan<sup>15</sup> and C. L. Baker.<sup>4</sup> The Georgia and Florida fuller's earth is thought to have been deposited as a calcareous clay in shallow Marine water. Activable earths are thought to be formed from the alteration of volcanic ash deposited as vitreous tuffs which were later devitrified.

*Theories of Behavior of Bleaching Clays.*—Bleaching clays were formerly divided into two groups widely different in properties: (1) the naturally active and (2) the activable clays. However, scores of clays having all intermediate degrees of behavior have been found and studied. A few samples showed bleaching power equal to the best fuller's earths and yet responded satisfactorily to acid activation. This gradation suggests that many fuller's earths were derived from bentonites (hydrated volcanic ash, low in silica) by natural leaching in surface water assisted in some cases by plant acids and bacteria, all of which have been found by laboratory tests to modify clays profoundly. Such an origin is further indicated by the presence of nearly pure bentonite at the bases of thick beds of some fuller's earth deposits in central Georgia and northern Florida. Ash deposited *in situ* became bentonite; that which gradually washed in, with leaching of grain surfaces, became fuller's earth, sometimes very free from silt.

After room-drying, lumps of bentonite slake readily in water; lumps of fuller's earth do not, or at most crack into large chips. The northern bentonites (Wyoming) swell and gel on slaking.

Samples of fuller's earth, on room-drying, change very little in bleaching power, usually improving slightly with the dehydration.

#### DISTRIBUTION OF DEPOSITS

Bleaching-clay deposits are well distributed throughout the world, but more clays and larger deposits have been found in the United States than elsewhere. Countries known to produce bleaching earths for clay consumption are: United States, England, Germany, Russia, France and Japan. Clays susceptible to activation to a high degree have been found

<sup>27</sup> References are at the end of the chapter.

in Germany and France and in the states of Arizona, Mississippi, California, Oklahoma, Texas, Florida, Georgia, Arkansas, Colorado and Utah. While natural bleaching earths are widely produced and distributed, there are relatively few places in the world where commercial activated clays are produced. United States and Germany are leaders in the world production of activated clay. A considerable quantity of the German product is used in the United States. Germany's natural advantages have been lower rates for labor, lower cost for acid used in the process, and extremely low freight rates to the United States. A protective tariff tends to equalize the cost of the German with that of the domestic product. Substantial quantities of natural clays are imported from England. However, here again the domestic industry is protected to some extent by the tariff. The known deposits of bleaching earth in the United States are more than sufficient to meet all conceivable requirements for years to come.

### PRODUCTION AND CONSUMPTION

Bleaching earth has been used in various ways for many centuries. Mention is made of it in the Bible and in the writings of Pliny. In modern times England has mined fuller's earth, and up to the twentieth century was practically the only source of the material. Fig. 1 gives the

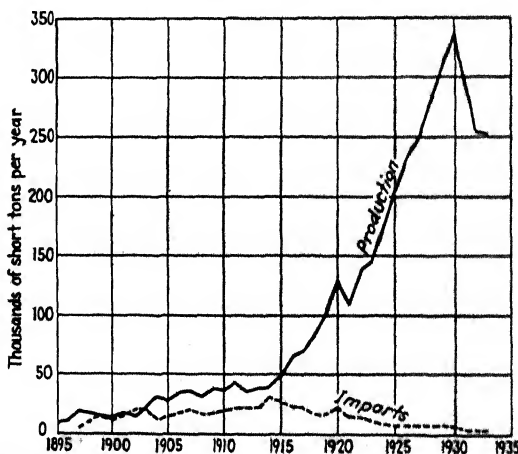


FIG. 1.—TRENDS IN PRODUCTION AND IMPORTS PER SHORT TON OF FULLER'S EARTH, 1895-1935.

After W. W. Adams and R. W. Metcalf: Fuller's Earth. Minerals Yearbook, 1934.

trends in production and imports per short ton of earth during the period 1895 to 1933. This chart indicates production of all naturally active earths, including fuller's earth but excluding activated earths. American production has grown rapidly in recent years, although for certain uses English fuller's earth is still brought into the United States.

Activated clay was manufactured first in Germany about 30 years ago, and in this country some 15 years later. The petroleum refiners were quick to see its value and now production has increased to the point where the United States meets most of its own requirements. The total world production of activated clay at the present time is believed to exceed 50,000 tons annually, about half of which is produced in the United States. As stocks are usually small, consumption corresponds closely with production.

Prior to the twentieth century bleaching clay was used chiefly for treating vegetable and animal oils. At present more than 90 per cent of the entire production is consumed in the petroleum industry. The consumption of activated clays has been greatest during the last decade. This type has been increasingly in demand on account of its high efficiency compared with naturally active clays. Even during the last five years, when there has been no increase in the use of other bleaching clays, the use of activated clays has more than doubled.

### PROSPECTING, EXPLORATION AND MINING

*Prospecting and Exploration.*—The United States Geological Survey has made a rather extensive study of bleaching earths in the United States and various publications give details as to the location and nature of deposits covered in these studies. The relatively low value of bleaching earth makes it of little interest to the individual prospector. Most of the large companies do this work as needed. Many samples are received by these companies from landowners, and if the tests show promising results the deposits are inspected and samples obtained by open-cut methods or by use of hand core drills. Since the quantity of naturally active and activable clays in the United States is far in excess of any conceivable demand, prospecting and exploration are limited to properties for which location and mining conditions are particularly favorable.

*Mining Methods.*—Mining of bleaching earths for the most part is by the open-cut method. The overburden, which ranges from 5 to 50 ft. in depth, is removed either by steam shovel or dragline to within approximately one foot of the top of the clay. The remaining foot of overburden is removed carefully by hand or mechanical means. It is the usual practice to lay out the area carefully before beginning work, so as to evaluate fully the quality and amount of material to be mined. Whenever possible, mining is done in dry weather, in order to avoid excess handling of moisture. When the clay strata are too deep for open-cut mining, a tunnel method is used, very similar to that used in coal mining.

Great care is taken in mining to eliminate foreign material such as limestone or other rock. The water content of clay as mined depends largely upon the location and type of clay. The amount of uncombined water in southeastern clays as mined is approximately 50 per cent by

weight, while in the Arizona and California clays it varies from 20 to 30 per cent by weight. In some instances the lump clay is hauled from the mine to the mill in mine dump cars, but when the distance is too great the material is generally transferred by truck and rail. When weather conditions permit, much of the water is removed from the clay by air-drying before it is transferred.

## PREPARATION FOR MARKET

### FULLER'S EARTH

When the bleaching earth is to be used in the natural state without activation or granulation, the preparation for market is comparatively simple. It is only necessary to pass raw lump clay through a crusher, dry the crushed clay by means of a gas, wood or oil-fired rotary drier, and finally to grind the dried clay to the desired size. Dust losses are insignificant, because little money is spent on the material. It is important to

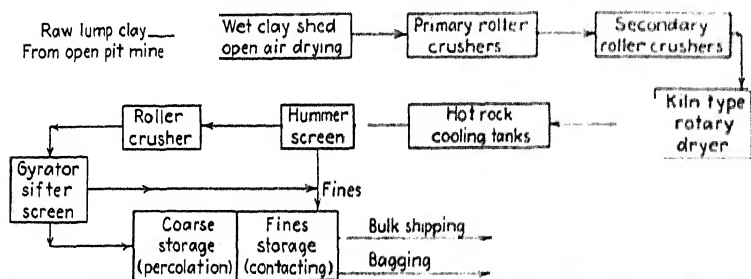


FIG. 2.—FLOWSHEET OF FULLER'S EARTH MANUFACTURE (PERCOLATION GRADE).

maintain careful technical control of temperature and time in the drying operation, because the clay can be injured greatly by incorrect handling. Experience has shown that a free moisture content of from 8 to 10 per cent gives the greatest efficiency for natural clays of the contact type. This corresponds approximately to a total volatile content of 15 per cent. The preparation of granular fuller's earth is somewhat more complicated.

The procedure in a typical fuller's earth plant in the United States is as follows: After the raw clay has been air-dried for two or three days, it is loaded into two portable distributors, each equipped with a hopper bottom and a steel-plate apron conveyor. The clay is fed at a uniform rate by the distributors onto a 24-in. inclined belt conveyor that discharges into two or more roll crushers which reduce the clay to a maximum size of 2 in. From the primary roll crushers it passes to bucket elevators that discharge it to five secondary crushers, which reduce it to a maximum size of 1 in. Oil-fired rotary driers housed in an adjoining building follow each set of crushers. The clay, in passing through a drier, is lifted by longitudinal interior channel irons and dropped through

hot gases. In the 20 minutes required for the clay to pass through a drier, its volatile content, including moisture, is reduced from 40 or 50 per cent to a maximum of 15 per cent. Chain drag conveyers of the bucket type move the product of the driers to three clay-cooling tanks which are well ventilated to carry off suspended dust, heat and moisture. By means of chain bucket elevators, the clay discharges into the top of the two tanks of larger diameter. Through a series of feed-regulating gate valves in the bottom of these tanks, it passes onto a conveyer belt, discharging into the top of the third tank, which has a hopper bottom and a mechanical feeder through which a uniform quantity of clay is fed to a  $\frac{1}{2}$ -in. mesh, electrically vibrated Hummer screen. The oversize, after being reduced in a high-speed roller mill, joins the undersize and passes directly to a belt conveyer equipped with a magnetic head pulley, which removes all tramp iron. The clay is then taken to the top of the mill building by a bucket elevator of the belt type, and passes in two equal streams on each side of a fire wall that is built on the center line of the building. Operations on each side of the wall are identical but distinctly separate from each other. The initial separation in the mill building is made by a Hummer screen of the same type employed under the clay-cooling tank. Reduction is effected in roller mills, which consist of duplicate sets of corrugated rolls. From each set of rolls the material is conducted to a silk-dressed gyrating sifter. Handmade silk of Swiss manufacture is used in these sifters. It is exceptionally uniform in quality, is durable and can be repaired readily. The oversize, or tailing, from each sifter passes directly to another set of rolls for further reduction and screening. This operation continues until the material has been reduced to the required mesh. After screening, the clay passes to a series of hopper-bottom bins, in which the various sizes are stored. Shipments are made in bags and in bulk.

For bag shipment the clay is weighed automatically and filled into bags of the best quality of burlap, usually 135 lb. to a bag. The bags are sewed shut, tagged, transported by hand truck to the shipping platform and placed in cars with the long dimension horizontal. Carloads consist of 25 to 35 tons. Bags are the property of the producer, and are credited on the consumer's account when they are returned in good condition. Milling practice in general is similar to that employed in milling wheat. The object of gradual reduction is to limit as much as possible the percentage of fines, the principal market demand being for the coarser or granular grades. Grain-type freight cars are used for both bag and bulk shipments.

#### ACTIVATED CLAY

The manufacture of an activated clay is more complicated than the manufacture of the granular fuller's earths (Fig. 3). There are seven

important steps in the process: (1) preparing the raw clay for charging to treaters or reaction vessels; (2) activating; (3) washing out impurities; (4) dewatering mechanically; (5) drying; (6) grinding to proper mesh size; (7) packaging.

The raw clay for charging to treaters may be prepared by either wet or dry method. When the wet method is employed water is added to the raw clay, which is already high in moisture, until it forms a slurry or thick slime, which is then conveyed to treaters by pumps or gravity. When the so-called dry method is employed, much of the free moisture is removed from the clay by a predrier. The dried clay is then usually conveyed by belts to a mixer, where water is added in order to make a slurry as it enters the treaters. Different methods are employed, depending upon the nature of the clay. Sometimes, instead of using ordinary water for making a slurry, a "sour" water or return liquor from the washing system is used. The clay and water, or liquor, are accurately measured before

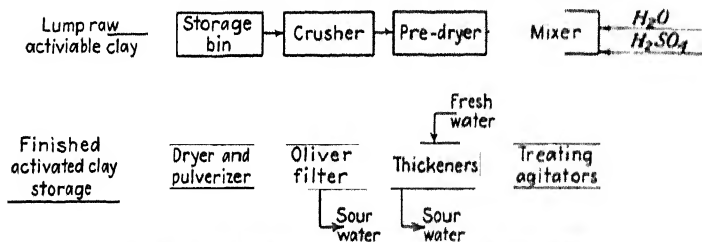


FIG. 8.—FLOWSHEET OF ACTIVATED CLAY PROCESS.

going to the treaters. The acids used for the activation are usually sulphuric or hydrochloric, generally sulphuric in this country, because of its lower cost. The acid is usually added to the slurry as it enters the treaters, although sometimes it is added during mixing or after the charge has entered the treaters. The proportion of acid varies according to its concentration and the nature of the clay. Steam is used to bring the charge to boiling point, and during the treatment the temperature is kept between 212° and 220° F. The charge is kept in constant motion during treatment by means of air or mechanical agitation. The length of time of treatment varies with the nature of the clay and the quantity and concentration of the acid; it is usually between 2 and 12 hours.

The so-called continuous method of treatment is sometimes employed. In this a proper mixture of the clay, water and acid moves in the form of a slurry from one treater to another in a series, as many treaters being used as are required to give the proper time for activation. All treaters must be made of or lined with corrosion-resisting materials.

After the activation has been completed, the slurry is conveyed to a countercurrent thickener system, where the water-soluble constituents are removed from the clay. A thickener system consists of a number of tanks

connected in series, one elevated slightly above the other. In each tank there is a shaft to which are attached at the bottom a number of rakes, usually four. The shaft is suspended in the center of the thickener and the rakes reach nearly to the outer edge. The speed of revolution of the shaft varies according to the settling rate of the solids. On the bottom side of the rakes are numerous blades set diagonally. As the solids settle they are dragged by the blades slowly to the center of the thickener, where they drop into a cone from which they are conveyed through a pipe line by means of a diaphragm pump, and discharged into the thickener next higher in the series. This operation is repeated through all thickeners of the system. At the same time there is uniform flow of fresh, soft, hot water entering the highest thickener of the system and moving down through the entire series, carrying with it a large part of the free acid, dissolved salts, and other impurities that have been separated from the solids. Sometimes the washing is done by means of filters and fresh water in a batch system and sometimes by filters connected in series in a continuous system. All pumps and lines used for conveying concentrated slurries must be of corrosion-resisting materials. For this purpose Duriron and lead have been very satisfactory.

From the thickener system the slurry is transferred either by pump or gravity to a continuous vacuum filter. The effluent is pumped away for further use in washing the slurry, or is discarded. The cake from the filter is conveyed to a drier, where its uncombined moisture is reduced to approximately 15 per cent. The dried material goes to a grinder and is pulverized to the size desired. Sometimes the drying and grinding are done in the same equipment. After the material has been ground it is usually packed by bagging machines into multiwall paper bags. Some bags are of the self-closing valve type, and others are of the open mouth type. When the latter are used the charge is weighed in the bagging machine and dropped into the bag and the closing is done by a sewing machine, which is part of the equipment. Multiwall paper bags have been used for activated clay during the entire life of the industry in the United States. They are used for shipments to all continents and are accepted by all classes of carriers.

Technical control of plant operations is essential at each stage in the process, in order to ensure a uniformly high quality of the final product.

### TESTS AND SPECIFICATIONS

The specifications for bleaching earths depend largely on the nature of the work to be done. For refining vegetable, animal and mineral oils by the contacting method, a finely pulverized clay is used, having a mesh of at least 50 per cent through 200 and generally 90 to 95 per cent through 200. The limiting factor on fineness is filter rate, or the speed with which the oil can be separated from the clay cake after contacting. If too much

impalpable powder is present, the filter rate may be retarded to a point unsuitable for refiner's use. Therefore, while it is an advantage from the standpoint of rapidity of decolorizing action to employ fine-mesh clay, the degree of fineness must be held within definite limitations. When the percolation method is used a coarse mesh is required in order to permit free passage of the oil through the clay. The most popular percolation grade is that known as 30/60 mesh. Other standard-mesh percolation grades are 60/90 and 15/30. Aside from meshing, the specifications for naturally active clays are very similar, whether they are contacting or percolation grade.

Table 2 gives typical physical tests of a naturally active commercial southeastern fuller's earth of fine and coarse grades, of western natural clay, and of fine-grade artificially activated clay. This table refers to physical tests only because the most important specification for a bleaching earth is its decolorizing value. A list of tests commonly applied in the bleaching-earth industry follow, together with a brief outline of each test:

TABLE 2.—*Typical Tests on Representative Clays*

Dry Natural Clay	Fuller's Earth, Florida-Georgia Type		Natural Bleaching Clay, Southwest Type, Fine Grade	Artificially Activated Clay, Domestic Type, Fine Grade
	Fine Grade (Contacting)	Coarse Grade (Percolation)		
Volatile matter, per cent.....	16.0	16.5	16.0	21.0
Density, lb. per cu. ft.....	31.0	35.0	53.0	36.0
Acidity, mg. KOH per gram....	Neutral	Neutral	Neutral	3.5
Screen test, per cent through 200 mesh.....	95.0		70.0	88.0
Mineral-oil decolorization value (efficiency $a = 100$ per cent), per cent.....	100		40-110	250-500

A. PHYSICAL AND CHEMICAL INSPECTION TESTS APPLICABLE TO BOTH NATURAL AND ARTIFICIAL ACTIVATED CLAYS.

**Volatile Content.**—The percentage loss in weight of a given sample of clay after ignition at 1800° F. for 10 minutes is known as the per cent volatile matter of the clay.

**Moisture Content.**—The percentage loss in weight of a given clay sample upon drying to constant weight at 220° F. is known as the moisture content of the clay.

**Volume Weight of Clay.**—The volume weight of bleaching-clay samples is determined by observing the volume occupied by a given weight of clay after five minutes mechanical tamping time, in a graduated cylinder, the results being expressed in pounds per cubic foot.

**Screen Analysis.**—A quantitative screen test is made on a given bleaching-clay sample by determining the weight per cent of clay retained by and passing through each of a series of standard measuring screens using the conventional Ro-Tap.



**Acidity.**—The bleaching-clay acidity comprises the weight of potassium hydroxide in milligrams required to neutralize a distilled water extract from one gram of clay, phenolphthalein being used as an indicator.

**Oil Retention (contact grade clays only).**—Oil retention characteristics of fine-mesh bleaching clays are determined by measuring the increase in weight of a given quantity of clay after contacting with oil and blowing the cake produced with air at 40 lb. per sq. in. pressure at a temperature of 375° F. Correction is made for any change in water content when calculation is made for oil retention.

**B. ACTIVATION METHODS.**—Natural bleaching clays, exhibiting potential activable characteristics, are activated by treatment in weak acid (i.e., 8% to 20%) at boiling temperature for six hours, washing the residual slurry free of acid and soluble salts, drying to 20 per cent volatile content and pulverizing the treated dry product.

**C. DECOLORIZATION TESTS.**

**Percolation-grade Clays.**—The decolorizing power of percolation-grade clay is determined by permitting a standard oil stock to pass through a column of granular bleaching clay and measuring the volume of filtrate obtained at a given composite filtrate color. By comparison of this yield with the volume of filtrate obtained under identical conditions through the use of a clay of known decolorizing power, it is possible to determine the efficiency of the unknown clay as compared with the standard.

**Contact-grade Clays.**—The decolorizing power of the contact-grade clays is gauged by determining the color produced by mixing the clay with a standard oil stock, agitating the mixture at a given temperature, and filtering the clay from the oil. Knowing the amount of a standard clay required to produce the same color, the decolorizing power of the clay being treated can then be expressed as per cent of the standard.

Since there is no single oil standard by which efficiency of the various earths are gauged, the relative values of competitive clays must be established on separate customers' stocks. The importance of oil-retention value of the competitive earths is second only to decolorization value, since the oil held up or absorbed in the clay after use is not customarily recovered and therefore the loss must be charged off to the operation when the clay is discarded. This particular test is not so important with the percolation-type clay, because revivification is generally practiced, but it is of utmost importance for contacting clays, where oil is frequently not recovered from the spent cake. A great advantage for chemically activated clays is the low oil retention, owing to the fact that only a small quantity of material is required to obtain decolorization.

#### MARKETING, USES AND PRICE

Fig. 4 shows a typical contact filtration plant for processing mineral oils with bleaching earth. This plant is semicontinuous and differs from the plants for bleaching vegetable and animal oils, which are generally batch operations. Fine-grade clay (100 mesh and up) is used exclusively in contact filtration plants. A typical percolation process for refining mineral oils is shown in Fig. 5. Among the principle types of oil refined

in the mineral-oil field are naphthas, fuel oils, lubricating oils, waxes and greases. The more important vegetable and animal oils to which bleaching clays are applied are cotton seed, soya bean, linseed, lard, coconut, palm and tallow.

The principal object of applying bleaching earths is to remove color, but there are increasingly important uses in all fields of refining that do not involve color removal. For instance, in treatment of naphtha gum

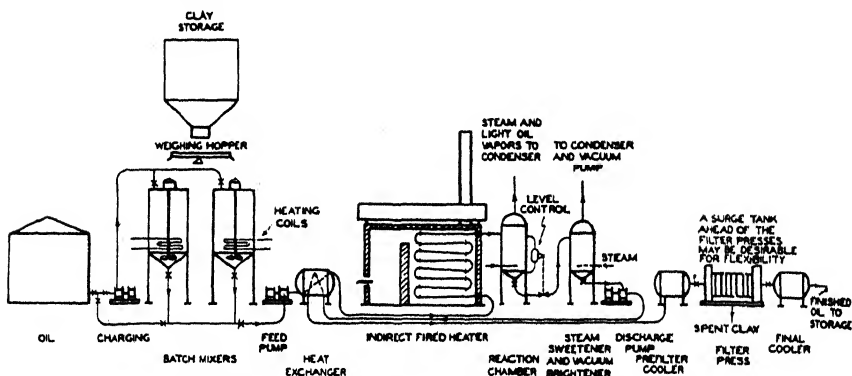


FIG. 4.—FLOW DIAGRAM FOR CONTACT FILTRATION PLANT.

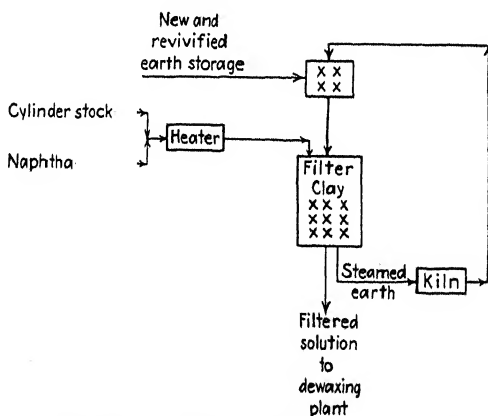


FIG. 5.—DIAGRAM OF MINERAL OIL PERCOLATION PROCESS (CYLINDER STOCK SOLUTION).

reduction and stability are more important factors than removal of color. In refining of lubricating oil improved sludge content, carbon content, oxidation test, acidity, emulsion test, viscosity index, etc., are often more important, and in the vegetable-oil field stabilization and removal of odor and taste are often the more important factors.

Some of the results secured with bleaching earths can be accomplished in part by other means of refining, such as solvent treating, acid treating, hydrogenation or fractionation, but the relatively low cost of the bleaching-earth process makes it extremely advantageous.

Deliveries of bleaching earth are made both in box and tank cars, but for the most part the clay is shipped in paper or burlap bags. On account of the wide variation in uses and type of equipment employed throughout the country, producers of bleaching earth maintain adequate staffs of experienced engineers to offer technical service to the customer.

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## BORAX AND BORATES

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**B**ORAX and boric acid are the two principal compounds of boron that are of commercial interest. Borax occurs in nature in an impure form. Formerly it was extensively manufactured from the lime borates, colemanite and ulexite, which are not soluble in water and require treatment with a solution of sodium carbonate to produce refined borax. The sodium borates, borax and kernite, however, are soluble in water and lend themselves readily to treatment.

The properties that render borax desirable and useful are its water solubility, low melting point, and fluxing properties. Its usefulness in these respects extends into many distinct fields.

Boric acid does not occur independently in nature in large quantities but is manufactured from borate minerals and salts. It is also obtained by condensation from natural steam in certain parts of Italy.

The development of borate mining in the United States has been featured by the successive discarding of one mineral for another that could be used more effectively. At first (1864–1872) native borax, or tincal, was obtained from lake muds. This source of supply was soon displaced (1872–1887) by ulexite and borax from the playas and borax marshes. As these deposits were of relatively low grade and erratic in their mode of occurrence, they were displaced (about 1887) by bedded deposits of colemanite in larger and purer bodies, together with associated massive ulexite. The later (1925) discovery of high-grade deposits of borax and kernite and the successful extraction of borax from the brine of Searles Lake again changed the source picture, and these sodium borates are now the chief source of supply for refined borax.

## COMPOSITION AND PROPERTIES

While the complete list of minerals containing boron is long—about 60 are known—only about half a dozen have been of much commercial importance. The important borate minerals in the United States that have served as source material for the preparation of refined compounds of

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boron are listed in Table 1. About two-thirds of all these important borate minerals, when calcined, consist of anhydrous boric acid ( $B_2O_3$ ).

TABLE 1.—*Important Borate Minerals of the United States*

Name	Formula	Percentage of Anhydrous Boric Acid ( $B_2O_3$ )	
		In Mineral	In Calcined Mineral
Borax.....	$Na_2O.2B_2O_3.10H_2O$	36.6	69.2
Kernite.....	$Na_2O.2B_2O_3.4H_2O$	51.0	69.2
Colemanite.....	$2CaO.3B_2O_3.5H_2O$	50.9	65.2
Ulexite.....	$Na_2O.2CaO.5B_2O_3.16H_2O$	43.0	66.6

Other borate minerals in the United States but of minor commercial value, and usually associated with those named in Table 1, are:

Tincalconite.....	$Na_2O.2B_2O_3.5H_2O$
Probertite.....	$Na_2O.2CaO.5B_2O_3.10H_2O$
Meyerhofferite.....	$2CaO.3B_2O_3.7H_2O$
Inyoite.....	$2CaO.3B_2O_3.13H_2O$
Priceite.....	$5CaO.6B_2O_3.9H_2O$
Bakerite.....	$8CaO.5B_2O_3.6SiO_2.6H_2O$
Howlite.....	$4CaO.5B_2O_3.2SiO_2.5H_2O$

In foreign countries, sassolite ( $B_2O_3.3H_2O$ ) and boracite ( $5MgO.MgCl_2.7B_2O_3$ ) have also been utilized commercially.

The term borax has been used loosely for almost any borate. The following synonyms have been used in the trade and in the literature instead of the correct and accepted names:

ACCEPTED NAME	INCORRECT SYNONYM
Borax.....	Tincal, prismatic borax, sodium biborate, sodium tetraborate
Tincalconite.....	Octahedral borax, mohaveite
Kernite.....	Rasorite
Ulexite.....	Boronatrocaltite, natroborocalcite, hayesine, franklandite, cryptomorphite, tiza, tinkalzit, borate of lime, cotton-ball, sheet cotton
Probertite.....	Boydite, kramerite
Priceite.....	Pandermite
Howlite.....	Pandermite
Boracite.....	Stassfurtite

The borate minerals chiefly produced in the different countries are as follows:

United States.....	Borax, ulexite, colemanite, kernite
Chile (also Argentina, Bolivia and Peru).....	Ulexite
Turkey.....	Priceite

Italy.....	Sassolite
Germany.....	Boracite
Tibet.....	Borax

Borax is found in individual crystals, as aggregates of poorly developed crystals, and as compact glassy masses showing no crystal faces. When pure, borax is clear and colorless but much of it is dull earthy white, because of partial dehydration to the lower hydrate tincalconite, and may be gray or dark colored opaque owing to enclosed mud. The crystals are monoclinic and have several cleavages, but the natural mineral seldom shows cleavage faces when broken. Its hardness is 2 to 2.5 and its specific gravity is 1.72. Borax is soluble in cold water but much more so in hot water. It swells and fuses when heated.

Kernite occurs in clear, colorless monoclinic crystals as much as several feet in diameter and in cleavable masses of similar size. Two perfect cleavages and several other planes of separation cause the mineral to break readily into small pieces and fibrous aggregates. The mineral somewhat resembles selenite gypsum in general appearance. The hardness is 2.5 and specific gravity is 1.95. Kernite is very slowly soluble in cold water but readily so in hot water. It expands when heated but does not swell as much as borax.

Colemanite occurs in shining crystals, colorless to white, and also as white to gray compact granular masses. Its hardness is 4 to 4.5 and specific gravity is 2.42. The mineral is insoluble in water but soluble in acids. When heated it decrepitates to a powder, a characteristic property.

Ulexite is not found in distinct crystals but forms either rounded aggregates of radiating acicular fibers (cotton balls) or solid masses of parallel or radiating white fibers with a silky luster. The hardness is 2 and specific gravity is 1.96 (not 1.65 as given in the textbooks). Ulexite is not soluble in cold water but is partly attacked by hot water and is readily soluble in acids.

#### ORIGIN AND MODE OF OCCURRENCE

The borate minerals described occur in sedimentary beds of different kinds, mostly clay and shale largely derived from volcanic ash, and associated with limestone and sandstone. To a large extent borax and ulexite result from the repeated evaporation of intermittent shallow lakes or playas which have received the saline-rich drainage from considerable areas. These deposits, including the well-known borax marshes, began to accumulate in Tertiary time and the mineral matter in them has been augmented in places by the boron-containing products from solfataras and hot springs, which represent the last stages of Tertiary and Quaternary volcanic activity.

The kernite of the underground deposits of the Kramer district in California is the product of recrystallization of earlier beds of borax. Its smaller content of water (26.3 per cent, as contrasted with 47.2 per cent in borax) indicates that it formed at a higher temperature than borax.

The lime borate colemanite occurs as geodes, nodules, small lenslike masses, bunched lenticular layers and compact beds of massive mineral. In many localities, colemanite was formed from ulexite by leaching. The leachings, containing soluble sodium borate, became a part of the general drainage, which in favorable places may have carried this material into lakes where subsequent evaporation produced beds of borax.

The boron originally came from solfataras and hot springs connected with past volcanic activity of the region where the borate minerals are now found. In whatever combination the boron first came to the surface, it has undergone many chemical and mineralogical transformations before final fixation in the bodies of borate minerals now found. Much of the boron was probably in the form of boric acid and first became fixed as ulexite ( $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ ) by the reaction of boric acid with the lime and soda derived from volcanic ash and clays resulting from the decomposition of the ash.

Later crustal movements have folded and crushed many of the borate beds and turned some of them on end. Different geological and mineralogical processes have altered the original structure of the sedimentary beds. Conditions have thus been favorable for a long continued series of mineralogical changes: first, the fixation of a boron mineral such as ulexite; next, leaching to form colemanite with release of water-soluble sodium borate. Borax with  $10\text{H}_2\text{O}$  changed to kernite with  $4\text{H}_2\text{O}$ , with later hydration to tincalconite with  $5\text{H}_2\text{O}$  and back again to borax with  $10\text{H}_2\text{O}$ . The lime borates form a similar series with changing water content, thus inyoite has  $13\text{H}_2\text{O}$ , meyerhofferite  $7\text{H}_2\text{O}$ , and colemanite  $5\text{H}_2\text{O}$ . The soda lime borates behave in the same way: ulexite has  $16\text{H}_2\text{O}$  and probertite  $10\text{H}_2\text{O}$ . Then come pseudomorphs of colemanite and meyerhofferite after inyoite, and of calcite after colemanite.

In all the known deposits of borax except the one at Kramer, Calif., other saline minerals, chiefly the chlorides, carbonates and sulphates of soda and of lime, together with other salts, are abundantly present. This is to be expected where such deposits are concentrations of salts brought in by drainage waters, augmented perhaps by evaporation products of boron-containing hot spring waters, which also contain similar salts in addition to borates. Searles Lake, with its wealth of chloride, carbonate, and sulphate saline minerals, is a typical example of such an association of borates with nonborate saline minerals.

The occurrence of borates of soda (borax and kernite) at Kramer, without the usual borate-free salines, therefore calls for an unusual expla-



nation. It is believed that the Kramer deposits of borax and kernite are neither simply the direct natural evaporation residues dissolved in and accumulated by surface or underground drainage waters nor are they direct deposits of hot-springs origin, but that they represent instead the concentration, evaporation, and in part, later recrystallization products, of the sodium borate leachings of ulexite, which forms in clay essentially free from the other much more soluble saline minerals named. Colemanite, formed by the leaching of ulexite, occurs abundantly in the western part of the Kramer area, where it was formerly mined. The first mineral crystallizing out of the sodium borate leachings was borax. Part of this was later recrystallized into the lower hydrate kernite, when the deposits were buried and subjected to increased temperature and pressure. Since the mines have been opened, part of the exposed kernite has changed back to borax by hydration.

The Kramer borate area in the western part of the Mojave Desert lies in southeastern Kern County, California, about halfway between Barstow and Mojave, and about 7 miles northwest of Kramer. The oval area in which the borate minerals (borax, kernite, ulexite, probertite and colemanite) have been found is 4 miles long in an east-west direction and 1 mile wide. Ulexite and colemanite seem to underlie the entire area but the sodium borates have been found only at three places in the central and eastern parts. Three mines in these places have produced borax and in two of them much kernite is associated with the borax. The beds containing the borate minerals occur in clays and shales in a synclinal basin of bedded Tertiary sediments, chiefly volcanic tuffs but with some limestone, chert, arkose, etc., resting on older granitic and metamorphic rocks. All the deposits are underground, mostly at depths between 325 and 900 ft. Alluvium covers much of the surface. It seems a curious irony of fate that the 20-mule teams, formerly trudging their weary way with their loads of borates from Death Valley to Mojave, passed almost over these immensely more valuable buried deposits. The old road lies only a few miles to the north.

No figures can be given as to the size of these deposits near Kramer, but in a report<sup>20</sup> published in 1929 the borate body in one of the mines is described as being about 100 ft. thick and extending at least 1500 ft. north and south and about 1200 ft. east and west. The production of crude borates from the Kramer area prior to 1935 is estimated as close to a million short tons. The Kramer area is capable of supplying enormous quantities of borates for many years.

Searles Lake, in the northern part of the Mojave Desert, is a roughly circular area of about 12 square miles, representing the accumulation of saline salts left by the gradual evaporation of a formerly much larger

<sup>20</sup> References are at the end of the chapter.

body of water. It is now a flat, white porous aggregate composed chiefly of crystalline salts of sodium and potassium permeated by a dense alkaline brine, and only during the winter does the brine sometimes rise a few inches above the surface. The total solids in the brine are about 36 per cent, as follows: sodium chloride 16, sodium sulphate 7, sodium carbonate 5, potassium chloride 5 and sodium borate 3.

### DISTRIBUTION OF DEPOSITS

The distribution of the deposits of borate minerals in the United States that have been worked is intimately related to the changing history of the development of the industry. This change is in large part due to the successive discovery and adaptation of different source materials (natural borax-ulexite-colemanite-brine-kernite and borax) used in the preparation of refined borax and other boron compounds. Therefore a brief historical outline is combined with that of the distribution of the deposits.

All the known or potentially commercial deposits of borate minerals in the United States are in the three western states, California, Nevada and Oregon. Priceite, a lime borate from Curry County, Oregon, and borax from Harney County, Oregon, have affected the borax industry but little. Total production from these deposits, just north of the southern boundary of Oregon, has been very small. California and Nevada therefore are the essential borate mineral producing states.

The first borax obtained in California (in 1856) was made by the evaporation of water from Tuscan Springs (later referred to as Lick Springs), 8 miles east of Red Bluff, Tehama County. Sodium borate was also found in solution in a number of springs in near-by counties. Very soon after the first discovery, crystals of borax were found in the muds of Borax Lake, in Lake County and the borax obtained there supplied much of that consumed in the United States from 1864 to 1868. For the next five years borax was recovered from the water and mud of near-by Hachinhama Lake. The discovery of large quantities of borax and ulexite in western Nevada and southern California in the early seventies brought to an end the first period of domestic production of borates.

Borax is reported to have first been found at Searles Lake, California, in 1862, although extraction from the surface efflorescences and underlying muds did not occur until about 1874. Borax is said to have been found in the flat basin of Death Valley in 1873, but commercial extraction began only about 1880.

In Nevada, Columbus Marsh was located in 1864 as a salt bed and the presence of ulexite was noted. In 1869 more "cotton balls" of ulexite were picked up and in the early seventies additional localities were found. Much activity in borax centered around Columbus Marsh in 1872-1873,

and the well-known marshes, Columbus, Teal, Rhodes, Fish Lake, and others, as well as Kane Springs in Kern County, Saline Valley in Inyo County, and other marshes in southern California, furnished cotton-ball ulexite and borax. In 1872-1874, carloads of ulexite from the Nevada marshes were shipped to Lake County, California, where it was treated with the sodium carbonate from Lake Hachinhama to form borax.

During the seventies and early eighties borax and ulexite from the lake muds of Nevada and California were the chief source of refined borax and this second period may be described as that of the borax marshes.

The discovery of colemanite as a new mineral in Death Valley in 1882 and in the Calico Mountains, San Bernardino County, the following year, ushered in the third period. For about 40 years, colemanite and associated ulexite from these and various localities in Inyo, Kern, Ventura, Los Angeles and San Bernardino Counties, and Clark County, Nevada, supplied much of the source material for the preparation of refined borax and other boron compounds. The mining of colemanite in massive beds many feet thick soon stopped the production of borax and cotton-ball ulexite from the surface efflorescences and muds of the marshes and dry lakes of the "borax lakes" and these were abandoned as source material about 1887.

Colemanite mining began in the Calico district, northeast of Daggett, about 1887, and the value of these deposits led to much prospecting and to the discovery of the massive commercial beds in the Death Valley region and elsewhere. Points of production changed as new deposits were opened. Colemanite was found near Stauffer, northeastern Ventura County, in 1898 and production ran continuously to 1907. The Calico district closed about 1907 and operations shifted to Ryan and Mount Blanco in the Death Valley region, to Lang in Los Angeles County, and to the Kramer district, Kern County, where colemanite and ulexite were discovered underground in 1913. The buried deposits of borax and kernite, about two miles to the east, were not discovered until 1925. Meanwhile operations in colemanite again shifted to near Shoshone, southeast of Death Valley, and to two deposits (White Basin and Callville Wash) in Clark County, southern Nevada. During this third or colemanite period, considerable quantities of ulexite were imported from Chile and to a lesser extent from Argentina, Bolivia and Peru.

The beginning of production of refined borax from the brine of Searles Lake in 1920 and the discovery of immense deposits of sodium borates (kernite and borax) in the Kramer district in 1925 soon closed the mines of the lime borates and the colemanite period saw its end. Today the Kramer and Searles Lake deposits of sodium borates furnish, and for some

time to come are likely to furnish, almost the entire supply of borax and other boron compounds for the world. The present (1934 and 1935) production of nearly a quarter of a million tons annually of borates from near Kramer and at Searles Lake has relegated all other deposits to a very insignificant position. Should a new use for colemanite be developed, other than as source material for refined borax, the deposits in California and Nevada could still supply a large demand.

The production of borate minerals in the United States has thus had four successive distinct periods, varying in location of source material and mineral composition of material mined. These may be summarized as follows:

First period.....	Northern California, 1864-1872	Borax
Second period (Marsh period)	Western Nevada and Southern California, 1872-1887	Borax and cotton-ball ulexite
Third period (Colemanite period)	Southern California and Southern Nevada, 1887-1926	Colemanite and massive ulexite
Fourth period.....	Southern California 1926 (Kramer and Searles Lake)	Borax, kernite, and brine

### PRODUCTION AND CONSUMPTION

From first production in about 1864 to 1883 (discovery of colemanite), the annual production was less than 3000 short tons of refined borax. For the next 15 years it varied between 3250 and 8000 tons per annum. Beginning with 1899, the annual production of crude borates increased considerably through 1913, fluctuating between 18,000 and about 60,000 short tons. Beginning with 1914, more than 60,000 short tons was produced annually, except for 1921 (50,000 tons). By 1923 both world and domestic production had reached a high figure, world production in that year being slightly over 200,000 short tons, a figure not again reached until 1933. Between 1923 and 1934 the annual domestic production ranged from 100,000 to 200,000 short tons, but in 1934 and 1935 production exceeded 200,000 short tons.

There has thus been a steady increase in the production of borates in the United States, with the present quantity far exceeding that of any previous time. No other country has shown such a steadily increasing output. The development of the two producing localities in California, both furnishing sodium borates, has adversely affected all other important deposits of borates throughout the world. Only the boric acid production in Italy has retained or improved its position.

In consequence, the percentage of domestic production to world production has increased from an average of 65 per cent for the years 1920 to 1928, inclusive, to an average of 93 per cent for the years 1929 to 1935. For both 1934 and 1935 the United States produced 95 per cent of all borates mined throughout the world.

The domestic and world production of crude borates for the years 1920 to 1935, inclusive, is shown graphically in Fig. 1.

For a long time Chile was the second largest producer of crude borates (ulexite), furnishing 55,000 short tons in 1913 and exceeding the production of the United States in 1908 and 1912, and nearly equaling it in other years. Argentina, Bolivia and Peru have produced much smaller quantities of ulexite (a few thousand tons annually). Production of crude borates from Chile declined rapidly after 1926 and production in South America practically ceased in 1929.

Turkey has been the third largest producer, furnishing about 10,000 short tons of priceite annually. Production declined about 1930,

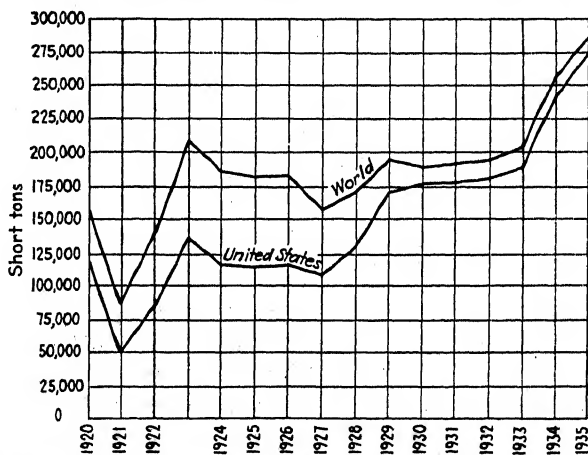


FIG. 1.—WORLD AND DOMESTIC PRODUCTION OF CRUDE BORATES, 1920–1935.

but, including 1934, amounted to 6000 to 7000 short tons annually. Italy has not only maintained its yield of 2000 to 4000 short tons of boric acid annually but since 1930 has increased it to between 5000 and 6000 tons. A total of about 1000 tons of borax from Tibet and boracite from Germany has been produced annually.

Around 1920 the apparent domestic consumption was about equal to domestic production. Beginning with 1923, exports of borax increased considerably, with a still further increase from 1927 on. From 1920 to 1926, inclusive, the United States consumed over 90 per cent of the domestic production. With the development of the present two producing localities near Kramer, and at Searles Lake, domestic production increased rapidly from 1928 on and exports likewise increased, so that from 1928 to 1935, inclusive, the apparent domestic consumption dropped to between 50 and 60 per cent of domestic production. This means that the two producing localities in California are supplying not only domestic requirements but nearly the entire world's demand for borax and related boron compounds.

## MINING METHODS AND PREPARATION FOR MARKET

Each of the three deposits of minable borates near Kramer consists of about one-quarter clay and three-quarters borate of soda. In the two deposits containing kernite, that mineral and borax are present in nearly equal proportions. Each of the deposits occurs as nearly horizontal tabular bodies or beds of borates parallel to the bedding of the enclosing clays and shales. After the shafts have penetrated the overburden the drifts and tunnels are cut in the borate bodies. In the one operating mine (1934) a regular set of drifts leads off from the main tunnels on the several levels and everything mined is borate. Considerable pillars are left for support but these are as rich as the material removed.

A selection either of nearly pure borax or of kernite (except for the ever present clay) could be mined, but it was found better to mine and grind the two minerals together. When crushed, kernite breaks into fine fibers, as the mineral possesses three cleavages in one zone. The granular borax prevents these cleavage fibers from clogging the grinders. The mixed borates are ground and roasted to remove water (26 per cent in kernite and 47 per cent in borax) and most of the clay is separated before shipment to Wilmington, Calif., for further refining.

On the basis of mineral composition as given above, the material mined should furnish about 90 per cent of refined borax by weight, without allowance for refining losses. The high yield is due to the fact that the change of kernite (with  $4\text{H}_2\text{O}$ ) to borax (with  $10\text{H}_2\text{O}$ ) consists in the addition of water, so that pure kernite, free from clay and other impurities, would yield theoretically 1.39 times as much borax. In actual mining procedure, it is not possible to obtain large quantities of kernite free from clay, and the advantage of having borax present for the grinding has already been mentioned.

After the discovery of borax at Searles Lake, a small plant operated intermittently until about 1895. In 1912 the production of potash salts and borax was seriously considered, and during the war years potash salts were extracted. Later, following an extensive program of research, the commercial production of borax from the brines was started in 1919, and in 1920 a total of 4643 tons of borax was produced, increased by 1926 to 17,500 tons and by 1930 to more than 50,000 tons.

At Searles Lake, the unusual chemical composition of the brine presented many operating problems and the physical chemistry of the equilibrium relations existing between the various salts in solution had to be worked out on the basis of temperature and concentration relationships. An extensive program of research was undertaken to obtain the fundamental knowledge of the relationships of these various salts,

necessitating changes in the previous manufacturing process and in equipment.

The process used for the production of borax, potassium chloride and other salts is essentially one of evaporation followed by fractional crystallization. The temperature and concentration of the brine must be accurately controlled throughout each step and the results obtained are an outstanding example of the usefulness and accuracy of the application of the results of physical-chemical research to industrial manufacturing problems.

After the brine is removed by wells sunk in the porous salt layer, it is mixed with the various end solutions from previous operations, and fed into evaporators or vacuum pans. The larger portion of the carbonate, sulphate, and chloride of sodium is precipitated during evaporation and removed. When the brine is nearly saturated with potassium chloride, it is rapidly cooled and the potassium chloride separates out. On further cooling, borax and other salts crystallize out, which by resolution and controlled cooling and crystallization yield pure borax.

#### USES AND PRICES

Borax is widely used for many purposes. Its easy solubility in water to a mildly alkaline and antiseptic solution, its low melting point and excellent fluxing properties make it one of the most useful of salts. Best known, perhaps, as a household commodity, it is of more importance in manufacturing industry, and many articles of everyday life require borax in their manufacture.

An excellent cleansing agent, it is widely used in industrial cleansing, as in washing, cleansing and laundering, either directly or as a constituent of soaps and soap powders.

Both borax and boric acid find many applications in medicine and pharmacy, as in disinfectants, mouth washes, tooth powders, cosmetics, lotions, ointments, deodorants and medicated lint and gauze.

Water solutions of borax are used to dissolve casein, which is extensively used in the manufacture of coated papers, playing cards, plywoods, plaster, paints and calcimines. The mild antiseptic character of borax prevents rancidity in cosmetics, pastes, glues, and various materials, and prevents the formation of mold or mildew in starches and sizes, of citrus fruits, leathers, textiles, etc. It is employed to retard the growth of certain fungi in lumber, and for fireproofing wood, paper and fabrics, for degumming silk, for neutralizing free acid in leather, and in dyeing leather and textiles. It hastens the cleansing of hides and skins and boric acid produces a soft, smooth grain in finished leather.

Its uses extend to baking powder, food preservatives, flavoring extracts, sirup and pickle manufacture, insect repellents, and many

others. Almost the whole line of manufacturing products finds use for borax, as in the manufacture of various kinds of implements, candles, carpets, drug specialties, dyes, hats, ink, jewelry, oil, paints, paper, stove polish, shoes, tobacco, tools, and many others.

Borax is an essential constituent of porcelain enamels, coating iron and steel as applied to kitchen utensils, stoves, refrigerators, washing machines, bathtubs, table tops, sinks, signs, pipe lines, tiles, and an endless array of products requiring an attractive, durable, and sanitary finish. The borax also facilitates the addition of coloring pigments to the enamels. In the manufacture of pottery, bricks, china, and both white and colored ceramic ware, glazes, and many kinds of glass, borax is indispensable, as it lowers the coefficient of expansion and makes the product more durable. Thus heat-resisting glasses are used in the kitchen and laboratory, for lamp chimneys, signal lenses, thermometers and optical glasses. In recent years the glass industry has become one of the largest consumers of borax, as it aids in the melting process and increases the strength, brilliance and durability of glass.

It is a good flux in the brazing, welding, soldering, etc., of metals, in assaying, in smelting copper and in refining gold and silver. Certain borides are good deoxidizers for nonferrous metal melts, such as brasses and bronzes. Ferroboron, in small quantities, is a deoxidizer for steel. Boron steels, with less than 2 per cent boron, are claimed to possess remarkable strength.

Boric acid, also water-soluble and antiseptic, is used in eyewashes, for hair waving, and other ways.

Borax glass, calcined borax, and anhydrous boric acid are also useful. Manganese borate is used as a drier in the manufacture of drying oils, linoleum, varnishes, printing and stamping inks. Ammonium borate is used in hair waving and certain types of electrolytic rectifiers and condensers. Boron carbide is extremely hard and is used as an abrasive. Sodium perborate is a useful disinfectant and solutions of it are used in dyeing and bleaching, and in electroplating.

Thus the cleanser, the pharmacist, the paper and textile manufacturer, the tanner, the potter, the enameler, the glassmaker and tilemaker, the metallurgist, the brazier, the jeweler, all use borax. Hardly any other substance enters into so many diversified lines of manufacture.

The value of the first refined borax produced from northern California ranged between \$700 and \$800 per short ton, or about 36¢ per pound. After the borax marshes of western Nevada and southern California began to produce, and the large deposits of colemanite were worked, the values of refined borax dropped rapidly, reaching a then low value of \$100 per short ton (or 5¢ a pound) in 1886, 1887, 1895 and 1896. No statistics on the value of refined borax are available for a number of



years but from 1914 to 1923 it varied from about \$80 to \$160 (in 1920) per ton. From 1920 on the value dropped, to \$30 a ton in 1931 and about \$35 a ton in 1935. From 1903 on, production and value of crude borate minerals is given, and this has ranged generally between \$20 and \$40 a short ton, with an average value of \$26 for the period 1920-1935. Since 1927 the value has not exceeded \$30 and for the last four years has been close to \$20 a ton.

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## CEMENT MATERIALS

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SO extensive has become the use of cement in highway and building construction in recent years that it has been suggested that the present stage of civilization be designated the "cement age." In this development and expansion of the cement industry quantitatively, qualitatively and geographically, numerous raw materials have been utilized. Some of these, used in the manufacture of highly specialized varieties of cement, find their chief application in other fields and are described elsewhere in this volume. This article therefore deals only with the raw materials of the puzzolan, natural and Portland cements.

## PUZZOLAN CEMENT

Puzzolan cement is so named from Pozzuoli, Italy, where a volcanic ash, called *pozzuolana*, has been dug, pulverized and mixed with quicklime to form a cement. This is one of the oldest cements known and was extensively used for roads and other structures at a very early date in Roman history. Similar volcanic rocks from other parts of the world have been used, especially in Europe. This type of cement possesses hydraulic properties by which it hardens or sets under water. The action of the quicklime on the volcanic products containing aluminum silicates produces lime silicates not unlike those of Portland cement. At a later date slags from the blast furnace were substituted for the volcanic ash, with satisfactory results.

The analysis of *pozzuolana* (volcanic ash) is:  $\text{SiO}_2$ , 44.50 per cent;  $\text{Al}_2\text{O}_3$ , 15.00;  $\text{Fe}_2\text{O}_3$ , 12.00;  $\text{CaCO}_3$ , 8.80;  $\text{MgCO}_3$ , 4.70; alkalies, 5.50; loss on ignition, 9.50. Puzzolan cements are variable in composition and in quality. Although some Roman objects of this material have survived hundreds of years, they are distinctly inferior to the modern Portland cement and are much more variable in chemical composition and in physical characteristics. A few years ago the writer had opportunity to examine some of the Roman cement baths discovered in the process of uncovering the ancient city of Pompeii. The cement showed no signs of deterioration and was actually harder than most of the natural stones of that region, although 2000 years old. For certain uses, puzzolan cements

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are perfectly satisfactory and are still used. Where they can be produced at low cost they will continue to be manufactured. In the United States their production has never assumed much importance.

### NATURAL CEMENTS

Natural cements are of more recent origin than puzzolan but antedate Portland by 68 years. Natural cement, as indicated by the name, is a product made by burning a clayey limestone in its natural state. John Smeaton, an English civil engineer, in 1756 found that "lime" made by burning an argillaceous limestone possessed the property of hardening under water. He stated that lime made from limestones containing from  $\frac{3}{14}$  to  $\frac{1}{17}$  of clay in "chemical combination" possessed these hydraulic properties. He said "it remains a curious question which I must leave to the learned naturalist and chemist, why an intermediate mixture of clay in the composition of limestone of any kind, either hard or soft, should render it capable of setting in water in a manner no pure lime I have yet seen, from any kind of stone whatsoever, has been capable of doing" (ref. 3, p. 3).\*

Smeaton's work led to many investigations and during the next 60 years a great many varieties of natural cements were manufactured in

TABLE 1.—*Analyses of Magnesian Limestones from Rosendale, N. Y., Used in Manufacture of Natural Cement*<sup>14</sup>

PER CENT

	1	2	3	4	5
SiO <sub>2</sub> .....	30.50	29.98	30.84	27.30	27.98
Al <sub>2</sub> O <sub>3</sub> .....	6.84	6.88	7.75	7.14	7.28
Fe <sub>2</sub> O <sub>3</sub> .....	2.42	2.50	2.11	1.80	1.70
CaCO <sub>3</sub> .....	84.38	83.23	84.49	85.98	87.59
MgCO <sub>3</sub> .....	18.00	17.80	17.77	18.00	15.00
Alkalies.....	3.98	7.10	4.00	6.80	7.96
Loss on ignition.....	3.78	3.13	3.04	2.98	2.49

England and France, and various patents were issued. Instead of a single type of stone, a number of combinations were employed. Usually clay or shale was mixed with limestone, chalk or marl. In most cases the burning was carried little beyond the temperature necessary for the elimination of the CO<sub>2</sub>, although some manufacturers increased the temperature almost to the point of fusion.

The earliest production of natural cements in the United States is associated with the construction of locks for canals in the early part of the nineteenth century. When the Erie Canal was dug in 1818-1819 a

\* References are at the end of the chapter.

successful search was made along the route for stone satisfactory for the manufacture of natural hydraulic cement, and a few years later, when the Lehigh Coal and Navigation Canal was built along the Lehigh and Delaware Rivers in Pennsylvania, similar rock was sought and cement plants were erected at several places. At Rosendale, N. Y., so much natural cement has been produced that the name "Rosendale cement" has become almost a synonym for "natural cement" and has been used in some instances to designate natural cements made in other places. Analyses of Rosendale limestones are given in Table 1.

Natural cements were made extensively in the Lehigh Valley and elsewhere long before Portland cement. Production continued after the establishment of the Portland cement industry, although steadily declining until at present it is of relatively little importance. Owing to the lack of control of the raw mixture as well as the degree of burning, the resulting product is variable and can find a market only when it can be sold at a substantially lower cost than Portland cement. In Table 7, it may be noted that the average price of natural cement in the United States in certain years is higher than that of Portland cement. This is explained by its proximity to the source of consumption and the greater distance to Portland cement plants. Transportation costs constitute a large part of the selling price of cement. This situation at present exists in comparatively few places. Nevertheless there are some who maintain that for certain specific purposes some of the higher grade natural cements possess distinct advantages over Portland cement.

Rock not suitable for the manufacture of Portland cement can be used in natural cements. In general, there is a higher percentage of silica and magnesia. Some stone that has been used is practically pure dolomite and in many cases the  $\text{MgCO}_3$  content runs from 20 to 35 per cent, whereas stone containing less than 10 per cent is demanded for the manufacture of Portland cement, and the lower the magnesia the more desirable it is. The silica likewise varies greatly in the rocks used for natural cements. In many it exceeds 20 per cent and occasionally rock with more than 30 per cent has been used.

It is evident that natural cements can be made over a wider area than Portland cement, since all argillaceous limestones suitable for the Portland variety are equally adaptable for natural cement as well as other rocks that are useless for Portland cement. For this reason the manufacture of natural cements still continues in some sections.

### PORTLAND CEMENT

Portland cement now amounts to over 99 per cent of the total annual cement production.

Joseph Aspdin, a bricklayer of Leeds, in the County of York, England, is credited with having been the discoverer of Portland cement. On

Dec. 15, 1824, he applied for a patent for a product which he described as follows:

My method of making a cement or artificial stone for stuccoing buildings, waterworks, cisterns, or any other purpose to which it may be applicable (and which I call Portland cement) is as follows: I take a specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle, or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan until the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into consistency of mortar, and thus applied to the purposes wanted.<sup>1</sup>

The product that Aspdin made was apparently a poor cement when compared with the Portland cement of today. He did not seem to recognize the importance of burning the mix to incipient fusion nor did he explain the meaning of "specific quantity of argillaceous earth, or clay," which indicates that the proportions of the ingredients were only roughly determined. Nevertheless, his Portland cement was an improvement on the other types of cement previously used. The name Portland was chosen either because the cement resembled Portland stone or it was intended as a substitute for that widely used building stone.

During the next 30 to 40 years, manufacture of Portland cement extended to other European countries; first to Belgium and then to France, Germany and Austria. Imports of Portland cement came into the United States in increasing amounts during the Civil War and later, and entered into competition with natural cements produced in several localities.

As the result of rather crude experimentation, David O. Saylor, a manufacturer of natural cement in the Lehigh Valley, Pennsylvania, in 1871 succeeded in making a product similar to the imported Portland cement. On Sept. 26, 1871, he received a patent on a process and product which he described as follows:

I have discovered that some kinds of the argillo-magnesian and also argillo-calcareous limestone found along the Appalachian range, containing more or less carbonate of lime, magnesia, silica, alumina, iron, salts, and alkalies adapted to the purpose, and which are now extensively used in the manufacturing of hydraulic cement, will make, when burned to a state of incipient vitrification, so as to be agglutinated, warped, or cracked, by contraction, and some burned to cinders, a very superior and heavy hydraulic cement, weighing from one hundred and ten pounds to one hundred and twenty pounds per bushel, and in every respect equal to the Portland cement made in England and imported into this country.<sup>11</sup>

Saylor's Portland cement was not always uniform and satisfactory but in 1876 at the Centennial Exposition in Philadelphia it received an "award of merit." Since that time the Portland cement industry of the United States has steadily progressed. The production has increased and the quality has been improved.

There have been a number of definitions proposed for the modern Portland cement, and from time to time the accepted definitions or specifications in different countries have been substantially modified. The definition accepted by the American Society for Testing Materials in 1933 is as follows:

Portland cement is the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination except water and calcined or uncalcined gypsum.

In addition there are a number of chemical and physical requirements.

#### CONSTITUTION OF PORTLAND CEMENT

A large amount of chemical and petrographic work has been done on Portland cement but there still remain many questions in regard to its chemical and mineralogical composition. It has been proved that it is a mixture of several compounds. The essential ingredients are  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ . These combine in the kiln to form silicates and aluminates, which at varying temperatures break down and recombine to form still other compounds. Rankin and Wright<sup>13</sup> have shown that a variety of products can be formed from these oxides alone or by varying combinations of two or all three. They list 26 different combinations, any one of which may develop, and give a table of optical and crystallographic properties. Some are stable only at certain temperatures whereas others are stable at all temperatures. At specific temperatures particular combinations result.

Only a relatively small number of these possible compounds have been identified in Portland cement. When the correct proportions of  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  are used and the mixture is properly burned, the clinker should be composed of tricalcium silicate ( $3\text{CaO}.\text{SiO}_2$ ), beta form of dicalcium silicate ( $2\text{CaO}.\text{SiO}_2$ ), and tricalcium aluminate ( $3\text{CaO}.\text{Al}_2\text{O}_3$ ). A number of the other combinations of the three oxides of Ca, Si and Al have been noted in finished Portland cement as well as the uncombined oxides.

Inasmuch as the rocks used in the Portland cement industries generally contain some iron, magnesia, alkalies, as well as other materials, naturally there are other compounds produced, some of which have received rather careful study.  $\text{MgO}$  does not readily unite with either  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  at the normal kiln temperature, so that it is regarded as an undesirable ingredient and consequently any appreciable amounts present in the raw

materials unfit the stone for use. A number of investigators claim that the  $\text{MgO}$  passes through the kiln and into the clinker entirely uncombined. This is disputed by others, who report the  $\text{MgO}$  entering into combination in similar manner to  $\text{CaO}$  and forming the compounds  $2\text{MgO}.\text{SiO}_2$ ,  $2\text{CaO}.\text{MgO}.\text{SiO}_2$ ,  $3\text{CaO}.\text{MgO}.\text{SiO}_2$ , and  $\text{MgO}(\text{Al},\text{Fe})_2\text{O}_3$ . The permissible limit of 5 per cent  $\text{MgO}$  has been fixed for the finished cement. In making a mix,  $\text{Fe}_2\text{O}_3$  can be substituted for  $\text{Al}_2\text{O}_3$ . For certain kinds of Portland cement rather large percentages of iron oxides are added to the mix instead of clay or shale. Normally there is some iron in almost all limestones, shales and clays. There are several iron compounds in which  $\text{Fe}_2\text{O}_3$  unites with  $\text{CaO}$  or with both  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ . The most common compound is tetracalcium alumino-ferrite ( $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ ).

The alkalis enter into chemical combinations to a slight degree. They are regarded as undesirable. Most of the potash appears to be volatilized and passes off through the stack. During the World War some cement plants installed apparatus to collect the flue dust for fertilizing purposes, because of its high content of potash.

Altogether the constitution of the various grades and types of Portland cement is still a fruitful field of research. A great deal of research work has been done in the chemical reactions that take place in the hardening or setting of cement and on the minerals developed. Most of the conclusions are highly theoretical and many are definitely in conflict. Kühl reaches the following conclusion as to the hardening process that takes place when water is added to the finished Portland cement:

It has thus been convincingly proved that, if we ignore the unimportant minor constituents, hardened cement mortar must be regarded as an unstable gel consisting of dicalcium hydrosilicate, tricalcium hydroaluminate, hydrated lime and calcium ferrites of unknown composition. All these ingredients tend slowly to pass over into the crystalline form, although this transformation requires a period of some years before it can be observed and some decades before it is complete. We are ignorant of the order in which the different gel compounds assume a microcrystalline structure. Probably the calcium hydroxide and calcium hydroaluminate are first affected, followed only at a later stage by the gradual transformation of calcium hydrosilicate.<sup>4</sup>

*Desirable Proportions of Ingredients for the Kiln Mix.*—It is not feasible to enter into a full discussion of the composition of the mix as it is fed to the kiln, inasmuch as there are so many varieties of Portland cement now being manufactured, each of which may have definite specifications. Since it is believed that the tricalcium silicate ( $3\text{CaO}.\text{SiO}_2$ ), which contains by weight 73.6 per cent  $\text{CaO}$  and 26.4 per cent of  $\text{SiO}_2$ , is the most important constituent of Portland cement, obviously rocks that can furnish these materials in somewhat this percentage might be regarded as most desirable. However, in practice this does not hold, as siliceous limestones cannot be used alone for the manufacture of Portland cement.

As a generalized statement, it may be said that the raw mix should contain about 75 per cent  $\text{CaCO}_3$ , about 20 per cent  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .



with about 5 per cent for the impurities such as magnesia, alkalies, etc. The silica should approximately equal the combined  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .

### ROCKS UTILIZED IN MANUFACTURE OF CEMENT

Since Portland cement is a cheap product, until recently it has not been economically feasible to break up different kinds of rocks, selecting the desirable materials and discarding the undesirable. Therefore the cement manufacturers have sought some natural rocks in which nature has combined the ingredients in the proper proportions for the best grade of cement. Failing in this, they have looked for a second kind of rock of such composition as to make up the deficiencies. Joseph Aspdin first used a mixture of Carboniferous limestone and alluvial clay and later

TABLE 2.—*Materials Used in the Cement Industry*

Source of $\text{CaO}$	Source of $\text{Al}_2\text{O}_3$	Source of $\text{SiO}_2$	Source of Fe
Limestones.	Clay	Clay	Limestones and marls
Calcareous marls	Shale	Shale	Clay, shale
Fossil-shell marls (bog lime)	Slate	Slate	Slate
Recent shells	Ash from coal used as fuel	Ash from coal used as fuel	Argillaceous limestones
Alkali waste	Argillaceous limestones	Argillaceous limestones	Iron ores
Blast-furnace slag	Blast-furnace slag	Blast-furnace slag	Blast-furnace slag
	Granite	Sand	
	Andesite	Sandstones	
		Granite	
		Andesite	

chalk and clay. The first Portland cement of the United States was by pure luck made of an argillaceous limestone that is well developed throughout the Lehigh Valley, and which has in many places almost exactly the requisite proportions of the necessary constituent minerals. Few regions are as well favored. Sometimes one finds a property where strata of different compositions can be quarried to make a proper mix. Other companies are required to obtain part of the necessary stone from fairly distant places. Since the finished product is cheap in price and the margin of profit small, it is not economically possible to pay freight charges on any considerable part of the stone.

When it becomes necessary to bring together two or more kinds of rock for the proper mix, the prevailing custom is to use a calcareous rock to supply the necessary calcium oxide and an argillaceous material for the alumina and silica. Sometimes a siliceous rock such as sand or sandstone

is used, bauxite when more alumina is desired and iron ores if a high-iron cement is produced. The list of materials given in Table 2 may not be absolutely complete, but it is believed to include all the sources that have been utilized to a large extent.

### LIMESTONES\*

A limestone may be defined as a sedimentary rock, normally white to light gray or buff in color, composed primarily of calcium carbonate ( $\text{CaCO}_3$ ) and occurring in beds or strata.

*Chemical Composition.*—From the normal type, there are many variations and in places limestones pass almost insensibly by gradation into shales or sandstones. No one has attempted arbitrarily to draw the lines separating the various classes of sediments. Instead, it is customary to use adjectives to describe the intermediate varieties. Thus we have siliceous limestones or calcareous sandstones and argillaceous limestones or calcareous shales. In addition, limestones containing abnormally large percentages of iron, phosphate, carbonaceous matter and magnesia are described respectively as ferruginous, phosphatic, carbonaceous and magnesian limestones. In some cases, the presence of ingredients other than calcium carbonate tends to make the limestones less valuable, but in others foreign matter renders them more useful for particular purposes.

A pure limestone should contain 100 per cent of  $\text{CaCO}_3$ , and there are a few that approximate this composition. Since virtually all our limestones have been laid down in shallow ocean waters in which there are various substances other than  $\text{CaCO}_3$  in solution and in suspension, it is to be expected that some of these will be precipitated on the ocean bottom.

In analyzing limestone, the substances usually determined are calcium oxide ( $\text{CaO}$ ) or calcium carbonate ( $\text{CaCO}_3$ ), magnesium oxide ( $\text{MgO}$ ) or magnesium carbonate ( $\text{MgCO}_3$ ), carbon dioxide ( $\text{CO}_2$ ), silica ( $\text{SiO}_2$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ), ferrous oxide ( $\text{FeO}$ ), sulphur ( $\text{S}$ ), sulphur dioxide ( $\text{SO}_2$ ), sulphur trioxide ( $\text{SO}_3$ ), phosphorus ( $\text{P}$ ) or phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), calcium sulphide ( $\text{CaS}$ ), strontium oxide ( $\text{SrO}$ ), hydrogen sulphide ( $\text{H}_2\text{S}$ ) and water ( $\text{H}_2\text{O}$ ). For individual purposes the analysis will not show nearly all of these. For example, a steel company may determine only the amount of silica and a cement company rarely determines other than the calcium, magnesium, silicon, iron and aluminum compounds. The substances occasionally determined are manganese dioxide ( $\text{MnO}_2$ ), titanium oxide ( $\text{TiO}_2$ ), carbon ( $\text{C}$ ), sodium oxide ( $\text{Na}_2\text{O}$ ), and potassium oxide ( $\text{K}_2\text{O}$ ).

It is recognized that all of these materials may and do vary widely in the amount present. It is not possible to state the limits definitely

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\* A portion of the general descriptions of limestone is taken from the author's *Limestones of Pennsylvania*, Bull. M20, Pennsylvania Geol. Survey 4th ser. (1934). 729 pp.

but in general the following ranges are believed to be approximately correct. The  $\text{CaO}$  is apt to vary from 22 to approximately 56 per cent in some of the purest limestones. These correspond to 39.29 and 100 per cent of  $\text{CaCO}_3$ . The  $\text{MgO}$  content may vary from 0 to 21.43 per cent. This corresponds to 0 to 45 per cent of  $\text{MgCO}_3$ . In a few instances the magnesium has been reported as even higher, which probably means that some is present uncombined with calcium carbonate. Some analyses of this kind known to the author, however, are regarded as of questionable accuracy.

The  $\text{Al}_2\text{O}_3$  varies from zero in the pure limestones to as much as 5 or 6 per cent, or occasionally more, in the argillaceous limestones used for the manufacture of Portland cement. By a still further increase of  $\text{Al}_2\text{O}_3$  and a corresponding decrease in  $\text{CaCO}_3$ , the rock becomes calcareous shale and is no longer appropriately called a limestone.

The  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  range up to several per cent in some of the ferruginous limestones. Seldom do the iron oxides exceed 3 or 4 per cent. However, in western Pennsylvania the Vanport limestone has been changed to siderite by replacement and all gradations can be found from high-grade limestone ( $\text{CaCO}_3$ ) to siderite ( $\text{FeCO}_3$ ). When the siderite undergoes oxidation, as it does readily, the resulting material is practically pure iron oxide. Locally limestones are found unusually high in pyrite. On analysis, the iron is apt to be reported as oxide and may be higher than given above. Any limestone with more than 1 or 2 per cent of iron oxide is apt to become brown or red on oxidation by exposure to the air.

The silica content in limestone is very important for many industries using limestone. It is determined in almost every limestone analysis and may be said to be present almost universally. In many of the purest limestones it constitutes much less than 1 per cent. It probably averages from 3 to 6 per cent, usually more in the dolomitic limestones than in the low-magnesium varieties. In the most siliceous limestones, silica constitutes about 50 per cent of the stone. In certain places the Loyalhanna limestone of Mississippian age passes by gradation into a true sandstone in which the silica constitutes practically the entire composition.

Sulphur is frequently noted in chemical analyses of limestones and occasionally it is reported as  $\text{SO}_2$  or  $\text{SO}_3$ . It is unusual to find more than 1 or 2 per cent of sulphur present and generally it is much less than 1 per cent. The sulphur present, although generally reported as uncombined, is almost altogether in combination as sulphides, principally pyrite ( $\text{FeS}_2$ ) or marcasite ( $\text{FeS}_2$ ), or as sulphates such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or strontium sulphate ( $\text{SrSO}_4$ ).

Phosphorus, reported as P or as  $\text{P}_2\text{O}_5$ , is generally negligible in limestones although commonly present in extremely small amounts. It is generally regarded as objectionable but the permissible amounts have not been satisfactorily determined. Its effect in fluxing stone is known,

but not in Portland cement and other manufactured products. Some unaltered limestones in Kentucky and Tennessee contain from 2 to 6 per cent of  $P_2O_5$ , according to report. One cement company is said to have had difficulty in producing a satisfactory grade of Portland cement, because of the large amount of phosphorus in the stone used.

The water content of limestones is extremely variable. In most cases the analyses are reported as water-free. The amount of carbon present also varies greatly. It may occur in sufficient amount to make the limestone black, yet because of the ease with which it is oxidized and eliminated in manufacturing plants, it is seldom determined even though it may constitute several per cent of the stone. The other constituents of limestones are almost invariably present in such small amounts, fractions of one per cent, that there is little occasion to regard them, and their presence does not affect the utilization of the stone.

*Mineralogical Composition.*—The chemical composition of a stone does not necessarily indicate the particular minerals present. The minerals are definite compounds and some of the chemical elements and combinations as reported in chemical analyses may enter into several different minerals. For example, the silica may, and usually does, exist mainly as quartz, which is pure silica, but in addition part of it is combined into various silicate minerals; sulphur may be present uncombined, but is almost always united with iron to form pyrite or marcasite, with some other metals to form other sulphides, or with metals and oxygen to form sulphate minerals. In a similar way, almost every substance determined by the chemist may enter into combination with other material to form a number of different minerals.

The desirability of a particular stone may depend upon the minerals present and often may not be determined by the chemical analysis. An illustration is furnished by pyrite and marcasite, both with the same composition ( $FeS_2$ ) and yet with many different properties. On exposure to moist air both will oxidize to form iron oxides and sulphuric acid but with different rapidity. Marcasite will decompose quickly and a stone containing a large amount may crumble in a short time because of this action, whereas pyrite undergoes such a change very slowly in comparison. Other illustrations might be presented to show the importance of knowing the mineralogical composition of a stone as well as its chemical constitution.

A great variety of minerals has been reported as occurring in limestones. The list in Table 3 is not claimed to be complete but doubtless it includes most of the minerals thus far recognized. Of these calcite is the only essential mineral of pure limestone, and calcite and dolomite the only essential ones forming dolomitic limestones.

*Methods for Distinguishing Calcite and Dolomite.*—It is frequently useful to determine whether a limestone is composed mainly of calcite or dolomite and if possible to do so in the field. As the chemical analysis

of limestone is expensive and requires time, attempts have been made to locate stone of the required kind with a minimum of chemical analyses. Considerable progress has been made, although most geologists feel that they must check their field determinations by occasional analyses. Several methods are in common use.

If dolomite is present in large amounts, frequently the amount by weight can be approximated by balancing in the hand, as dolomite is slightly heavier than calcite. Of course, this method requires experience and at best is a rough determination. The color is apt to be suggestive in materials low in iron and carbonaceous matter. The more highly magnesian limestones show a light bluff tinge whereas the low-magnesia varieties are white or bluish gray. On weathering, however, the dolomitic layers become chalk white, considerably whiter than the low-magnesia strata.

The different degrees of solubility are more reliable in that calcite dissolves fairly readily in cold dilute hydrochloric or acetic acid and produces vigorous effervescence, while dolomite dissolves and effervesces very slowly in comparison. However, if the dolomite is pulverized by the blow of the hammer or if the rock is feebly cemented, and hence porous, this test is not serviceable because the effervescence may be almost as rapid and vigorous as in the low-magnesia rocks.

The low-magnesia limestones are soft and easily broken in comparison with the highly dolomitic ones, so that a geologist can with practice rather closely approximate the magnesian content by the hardness and toughness of the stone when struck with the hammer. The dolomitic stones are also finer grained and more compact than those lower in magnesia of the same region.

When weathered surfaces are available the distinctions between high-magnesia and low-magnesia limestones can readily be made. The high-magnesia limestones contain numerous straight cracks running in all directions, along which vein material has commonly been deposited in layers so extremely thin that the freshly broken surface scarcely indicates their existence. On being exposed to weathering agents, these cracks furnish access to dissolving fluids, and the weathered surface of the rock looks as though someone had hacked the stone with a steel-cutting implement. Where high-magnesia and low-magnesia limestones are interbedded, the contrast on weathered surfaces is striking. There is also a greater tendency for dolomitic limestones to show a distinctly granular surface on weathering.

Where interbedded high-magnesia and low-magnesia limestones have been deformed by folding, the dolomitic limestones have many more gash veins of quartz and calcite than do the purer limestones. There is also commonly a greater proportion of quartz in the vein fillings of the dolomites in comparison with calcite and dolomite.

Where weathering has progressed downward to considerable depth, the dolomites in various places of great crustal disturbances appear to be shattered as though by a blast of dynamite. One quarry, near Lancaster, Pa., in a highly dolomitic limestone region, was worked for road metal by means of a steam shovel without any blasting.

The highest grade of limestones, composed almost entirely of calcium carbonate, can be found in certain regions by noting the sinkholes and caves, caused by their ready solubility or by heavy clay overburden. In such instances, outcrops are apt to be few.

All of these shortcuts to the determination of the chemical composition of limestones by means of physical characteristics are useful, but must be used with care, as the most expert geologists in this line occasionally go astray, especially on entering a new region.

Since froth flotation has been used in the cement industry it has become important to know of the limestone minerals that have been reported. The list in Table 3 is fairly complete and includes a number that at present seem to have little economic importance.

TABLE 3.—*Minerals of Unmetamorphosed Limestones*

Carbonates	Silicates
Calcite ( $\text{CaCO}_3$ )	Feldspars
Aragonite ( $\text{CaCO}_3$ )	Albite ( $\text{NaAlSi}_3\text{O}_8$ )
Dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ )	Microcline ( $\text{KAlSi}_3\text{O}_8$ )
Siderite ( $\text{FeCO}_3$ )	Micas, especially muscovite or sericite [ $\text{H}_2\text{KAl}_2(\text{SiO}_4)_2$ ]
Ankerite [ $\text{CaCO}_3 \cdot (\text{Mg, Fe, Mn})\text{CO}_3$ ]	Tourmaline (complex silicate of boron and aluminum with magnesium, iron or alkali metals)
Oxides	Garnet (andradite type) [ $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ ]
Quartz ( $\text{SiO}_2$ )	Glauconite (ferric potassic silicate of variable composition)
Chert, flint, basanite, chalcedony, etc. (all are composed of $\text{SiO}_2$ )	Staurolite ( $\text{HFeAl}_2\text{Si}_2\text{O}_{11}$ )
Hematite ( $\text{Fe}_2\text{O}_3$ )	Hornblende (complex silicate containing Al, Fe, Mn, Mg, Ca, Na and K)
Limonite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ )	Hypersthene [ $(\text{Fe, Mg})\text{SiO}_3$ ]
Turgite ( $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )	Sulphates
Goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )	Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )
Pyrolusite ( $\text{MnO}_2$ )	Barite ( $\text{BaSO}_4$ )
Rutile ( $\text{TiO}_2$ )	Phosphates [ $\text{Ca}_3(\text{PO}_4)_2$ , $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , etc.]
Titanite ( $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ )	Fluorides
Zircon ( $\text{ZrSiO}_4$ )	Fluorite ( $\text{CaF}_2$ )
Cyanite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ )	Carbonaceous or bituminous matter
Sulphides	Hydrocarbons and carbon
Pyrite ( $\text{FeS}_2$ )	
Marcasite ( $\text{FeS}_2$ )	
Galena ( $\text{PbS}$ )	
Sphalerite ( $\text{ZnS}$ )	
Chalcopyrite ( $\text{CuFeS}_2$ )	

Of the minerals constituting the unmetamorphosed limestones, only a few are readily visible usually. The others are recognized only when they possess distinctive colors or when the carbonates are dissolved by

acid and the residues are examined microscopically. The microscopic examination of residual insoluble materials has become in recent years a fertile field of research and has shown the presence of many minerals not previously suspected to exist in limestones.

The minerals present in unaltered limestones belong to three classes as to origin: (1) minerals precipitated from solution either by organic agencies or by chemical inorganic precipitation; (2) minerals that have been carried into the ocean by the land waters in suspension and have been dropped into the calcareous oozes; and (3) minerals that have been introduced into the oozes or consolidated limestones in solution by infiltrating waters at some subsequent time. It is not easy to classify the minerals into these three groups, for it is known that some of them occur in two or possibly all three divisions. Nevertheless, it is well to recognize the different origins.

Of the minerals precipitated from solution, calcite is the most important. Practically all the calcite has been carried into the ocean in solution and there has been precipitation by chemical reactions or abstracted from the water by organisms and built into their structures, which later collected in the ocean bottom. Most of the dolomite and silica, as well as the whole group of easily soluble minerals, were doubtless precipitated in a similar way. In regard to many others, even including the silicates, there is still considerable doubt as to whether they may not have been formed in some places by precipitation from solution contemporaneous with the formation of the calcareous ooze.

Of those carried into the ocean in suspension, we may include virtually the entire list of limestone minerals, although it is probable that only small quantities of the more soluble ones were transported from the lands to the seas except in solution. The oxide and silicate minerals in the main are relatively insoluble, so that most of them will be left on the surface in the decomposition of crystalline rocks in which they are most abundant, and are then apt to be picked up by surface streams, carried in suspension and eventually reach the sea. The indications are that limestones have been formed in places where only particles of small size derived from the lands could have been carried. Such a condition may exist near shore as well as far from land. This means that land-derived minerals can seldom be detected except by microscopic examination. Occasionally layers are found where the particles are large enough to be readily distinguishable with the naked eye. Most limestones on casual examination appear to be free from foreign minerals and yet even the purest are found to contain small particles when the residues are studied after the solution of the carbonates by acid. In regions where deposition was near an area of igneous or metamorphosed rocks, the variety of minerals present is surprising. Most of them show evidences of rounding by attrition during transportation or pitting by corrosive action.

Many of the minerals present in limestones are of secondary origin, having been introduced by water circulating through the pores and larger cavities at a period following deposition of the oozes and continuing even after consolidation of the original sediments. It is generally believed that these new minerals are introduced by water considerably above the temperature of shallow meteoric or surface waters, such as would be found in deep-seated waters, although there is some evidence to support the belief that this process at times takes place at shallow depths. When the calcareous sediments have been buried beneath hundreds or thousands of feet of later deposits, there is no doubt that the circulating waters, regardless of their original source, are higher in temperature and have a decidedly higher mineral content, and hence do more work of introducing new minerals. Further, such waters do much work of concentration of the ingredients finely distributed throughout the original oozes. At one time it was believed that most of the silicates, among them the feldspars, could be formed only at high temperatures, but there are a number of cases tending to show that feldspars have formed in limestones that have never been subjected to high temperatures such as are necessary for the formation of most of the metamorphic minerals.

The metamorphosed limestones contain a greater variety of minerals than do limestones not so altered. Further, the minerals present are generally in larger grains. In addition to the minerals already listed, the following have been observed: sulphur, graphite, magnetite, corundum, emery, spinel, pyrrhotite, chalcocite, molybdenite, apatite, phlogopite, biotite, tremolite, actinolite, epidote, olivine, talc, serpentine and others of rare occurrence.

In many places the limestones have been subjected to such intense compression by mountain-building forces that the temperatures of the rocks and the circulating waters were sufficiently high to cause important mineral changes. At others, the limestones have been intruded by molten igneous matter, which has caused similar heating and new combinations. The minerals formed under either of these conditions are known as metamorphic minerals, and constitute a large group. In the metamorphism of calcareous rocks the greatest change is that of recrystallization by which marbles are formed from the original limestones.

The oldest limestones have been subjected to great earth pressures at several different periods and contain many metamorphic minerals, whereas the youngest limestones have been little disturbed and have few metamorphic minerals. Even in rocks of the same age, some are found in regions of former great disturbances and consequent heating, whereas in other sections such forces have never been exerted on the rocks. The pre-Cambrian limestones, as a result of greater age and more compression, contain many of the minerals listed above, the Paleozoic limestones have suffered less compression and have few new minerals, and Mesozoic and



Cenozoic limestones in most sections are practically devoid of metamorphic minerals.

*Physical Properties.*—The physical properties of the limestones, such as color, odor, texture, structure, hardness, toughness, specific gravity, porosity, strength, etc., are of little importance when the stones are used for the manufacture of cement. The structures may facilitate or interfere with quarrying and the textures may likewise have some effect on the crushing, but these conditions apply to all types of rocks.

*Origin.*—A discussion of origin of limestones is of importance in this chapter only because it helps to explain their variable character, a condition that confronts many cement companies. Limestones are primarily of organic origin, in that the  $\text{CaCO}_3$  has been abstracted from the ocean waters by organisms, either plant or animal. Some of these organisms use the carbonate in their structures but others precipitate it outside their bodies by chemical reactions resulting from their life functions. Other limestones are of inorganic origin, the precipitation having been effected by evaporation, concentration, pressure and temperature changes, etc.

The places of origin are varied, as limestones have been formed in fresh and marine waters and in shallow and deep basins. Accumulating evidence seems to indicate that the bulk of our limestones, except the argillaceous varieties, has originated in shallow marine waters near low-lying flat shores, to which little mud was being carried. Wind-blown dust and sand are present, sometimes in appreciable amounts.

Anyone familiar with the deposits of our ocean shores realizes the variable characters of the sediments. Likewise, the operators of many of the limestone quarries recognize the varying chemical composition of the successive beds of rock, and even the variations within short distances of rock of the same bed. These are due to the changing conditions of deposition in shallow water.

*Limestones Adapted to Cement Manufacture.*—For natural cement there is little need for careful choice of limestone—high and low magnesian as well as otherwise pure and decidedly impure limestones have all been utilized, either alone or mixed with other stones—but a different situation prevails if Portland cement is to be manufactured.

Perhaps the most common objectionable constituent of limestones for Portland cement is magnesia. Our pre-Cambrian and Paleozoic limestones generally contain considerable  $\text{MgCO}_3$ . Since this is converted into  $\text{MgO}$  in the kiln, and may remain in part inert, it is evident that its presence tends to decrease the strength of the cement. Standard specifications permit only 5 per cent in finished cement. This means that limestones containing upwards of 10 per cent  $\text{MgCO}_3$  are useless unless they can be mixed with enough other stone low in magnesia to bring the average down to the specified limit.

Other objectionable features of limestones for Portland cement are improper ratios of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ , although these can now largely be overcome by beneficiation, which is described on a later page.

Desirable features of limestone are such mixtures of the requisite ingredients that little or no correction need to be made by the addition of other types of rock. Argillaceous limestones such as occur in the Lehigh Valley, Pennsylvania, and in some other places possess a distinct economic value over other types of limestone. They are fine grained and the proportion of calcareous, aluminous and siliceous constituents is fairly uniform, so that it is relatively easy to obtain a mix. Some of these limestones contain slightly too much  $\text{CaCO}_3$ , so that at times some clay

TABLE 4.—*Analyses of Typical Limestones Used in Portland Cement*  
PER CENT

	Ordovician (Jacksonburg) Argillaceous Limestone, Lehigh Valley	Pennsylvanian (Allegheny-Vanport) Limestone, Butler Co., Pa.	Ordovician, Annville, Lebanon Co., Pa. <sup>a</sup>
$\text{SiO}_2$ ....	13.44	1.64	2.52
$\text{TiO}_2$ ....	0.23		
$\text{Al}_2\text{O}_3$ ....	4.55	2.20	1.56
$\text{Fe}_2\text{O}_3$ ....	0.56		0.55
$\text{FeO}$ ....	0.88		
$\text{MnO}$ ....	0.06		
$\text{CaO}$ ....	41.84	53.62	
$\text{CaCO}_3$ ..	71.71	95.76	94.44
$\text{MgO}$ ....	1.94	0.86	
$\text{MgCO}_3$ ..	4.07	1.82	0.90
$\text{Na}_2\text{O}$ ....	0.31		
$\text{K}_2\text{O}$ ....	0.72		
$\text{P}_2\text{O}_5$ ....	0.22		
S.....	0.33		0.015
C.....	0.75		
$\text{CO}_2$ ....	32.94	42.30	
$\text{H}_2\text{O}$ ....	1.55		

<sup>a</sup> High-grade limestone shipped to Portland cement plants in the Lehigh Valley.

must be added, but more generally they are deficient in lime and it is necessary to bring in some high-grade limestone from other places.

*Chalk*.—In some places, particularly in the southern part of England, northeastern France, and Belgium, chalk has been used in the manufacture of Portland cement instead of ordinary limestone. Chalk is merely a fine, soft, friable limestone that was extensively developed both in Europe and in the United States during the Cretaceous period. Its use in cement is not unlike that of the more ordinary limestones except that it can be both quarried and ground more readily. In general the  $\text{CaCO}_3$  content is very high, although in places it contains appreciable amounts of clay

and irregular flint nodules. The chalk mainly used contains from 88 to 96 per cent  $\text{CaCO}_3$ .

### MARLS

*Calcareous Marls\** (*Bog Lime*).—In many limestone regions, or in places where glacial deposits contain ground limestone or limestone pebbles, the ground and surface waters may be sufficiently high in dissolved lime to support lime-secreting plants and animals. Algae are the most important organisms in the extraction of the calcareous matter. In a limestone valley in Lancaster County, Pennsylvania, blue-green algae living in a small stream have formed a deposit of calcareous nodules of

TABLE 5.—*Analyses of Michigan Calcareous Marl*

	Wolverine Portland Cement Co.			
	Light Marl Dried	Blue Marl Dried	From Alpena, Mich., Dried	From near Grayling, Mich., <sup>a</sup> Dried
$\text{CaCO}_3$ .....	93.75	91.34	74.48	87.00
$\text{MgCO}_3$ .....	2.42	0.77	0.50	0.91
Soluble $\text{SiO}_2$ .....	0.18	0.42		0.13
Insoluble $\text{SiO}_2$ .....	1.01	.78		0.78
$\text{Al}_2\text{O}_3$ .....	0.55	.55	0.54	0.07
$\text{Fe}_2\text{O}_3$ .....	0.25	0.40	2.36	1.30
Moisture.....			1.25	0.60
Organic matter.....			12.88	9.80
$\text{SO}_3$ .....	Tr.	0.26	0.89	0.27
Alkalies and rest (by difference)	1.84	5.79		

<sup>a</sup> Sample lost 61 per cent of its moisture when dried.

sufficient thickness to have been worked on a small scale for agricultural lime. A maximum thickness of 8 ft. has been found.<sup>15</sup>

Conditions are seldom favorable in streams for deposits of such calcareous deposits of commercial importance. In lakes and marshes the situation is different and there deposits from 15 to 30 ft. thick, or even more, have accumulated. In the glaciated sections of the country there are scores of lakes where this material has formed since the withdrawal of the ice. The marl is dark gray to white, depending on the amount of organic matter present. Clay and sand are mixed with the calcareous matter, so that in purity it varies from practically pure  $\text{CaCO}_3$  to clay or sand with only a small percentage of lime. Naturally, the impure varieties are useless. The origin of the marl is attributed largely to the action

\* There is valid objection to the use of the term "marl" in this sense and "bog lime" may be regarded as preferable. However, since "marl" is the name used by the cement industry, it seems advisable to follow that usage.

of a water plant known as *Chara*, although blue-green algae and mollusca are also important. The  $\text{CaCO}_3$  coats the stems of plants in the lakes and is dropped on the bottom. In a few deposits the shells of small pelecypods and gastropods constitute the major portion, although this is rare.

In Michigan, these calcareous marl deposits are of great importance and have been worked in many places to supply the calcareous matter for Portland cement. The marl is readily dredged from the ponds, or if the ponds have dried up or can be drained it is easily dug. As dredged it contains from 25 to 50 per cent of moisture. When dry the marl is very light and porous. Although the supply in any one deposit is seldom large, there are so many of these marl lakes that an extensive cement industry has been established on this type of material. Clay is mixed with the marl to produce the requisite mix. The analyses in Table 5 are chosen from an elaborate report of the Geological Survey of Michigan.<sup>5</sup>

TABLE 6.—*Analyses of Shell Marls*  
PER CENT

	From Chuckatuck, Va.	From Yorktown, Va. <sup>a</sup>	From Grove, Va.	From Trent River, N. C.	
				Unwashed	Washed
$\text{SiO}_2$ .....	7.24	9.85	5.81	32.86	9.30
$\text{Al}_2\text{O}_3$ }	4.92	2.07	1.18	2.64	1.16
$\text{Fe}_2\text{O}_3$ }		2.88	0.62		
$\text{CaCO}_3$ .....	85.13	78.20	89.48	63.47	88.26
$\text{MgCO}_3$ .....	trace	0.28	0.96	0.36	0.38
Moisture.....		1.98	1.37		

<sup>a</sup> Average of samples from 15-ft. thickness of marl.

*Shell Marls.*—The Tertiary formations of the Atlantic Coastal Plain contain extensive deposits of fossil shells in a matrix of shell fragments, clay and sand. These are especially well developed in Virginia, North Carolina and South Carolina. They are flat-lying beds ranging in thickness up to 20 ft. or more and in most places are exposed at the surface or thinly covered by loose sands or clay. Another favorable factor is that in a number of instances these deposits are located on or near tidewater. Four cement companies have been organized in Virginia and North Carolina to exploit deposits of this character for the purpose of manufacturing Portland cement. The only plant built and in operation is owned by the Lone Star Cement Corporation, which dredges the shells from an extensive pit at Chuckatuck, Va., close to the James River, a short distance above Norfolk. The shell material is crushed, loaded on barges and taken to the plant in West Norfolk. The clay is obtained from a deposit a short distance farther up the James River. The material consists mainly of rotten molluscan shells but with representatives

of several other groups of organisms, especially corals. No difficulty is experienced in getting a satisfactory mix.

At Grove, Va., along the James River, at Yorktown, Va., along the York River, and near Newbern, N. C., along the Trent River, similar shell deposits have been investigated but no cement plants have been built. At times the shells have been dug for fertilizing purposes. Many other deposits of similar character have not been prospected. In places the sand and mud are objectionable, but generally they can be eliminated in large part by washing and screening.

*Recent Shells.*—Here and there along the Atlantic, Gulf and Pacific coasts there are deposits of recent shells, some on land and some beneath the shallow ocean or estuarine waters. Some of the land deposits are known as "kitchen middens," as they are composed of the oyster shells and clam shells discarded by the Indians. In some places these are sufficiently extensive to have been utilized for burning lime but do not contain enough material to warrant the erection of a cement plant.

Underwater deposits of modern oysters and clams are more extensive and have been investigated in several places. The best of these known to the author is the deposit being worked by the Pacific Portland Cement Co. at Redwood City, Calif. A deposit of loose oyster shells covers a large area along the west side of San Francisco Bay. The shells are mainly entire, detached, fairly fresh in appearance and range in size up to  $1\frac{1}{2}$  in. long and  $\frac{3}{4}$  in. wide. A few clam shells are present. No living oysters are known in the immediate section, so it is difficult to account for the great accumulation of these shells. In places the deposit is 30 ft. deep. They are contained in a matrix of fine blue mud. The shells are dredged, loaded on barges and taken to the plant for crushing and grinding. A mix can be readily obtained from the shells and attached mud. If there is too much mud, the excess can be eliminated by washing.

#### ALKALI WASTE

One of the waste products of alkali plants is precipitated calcium carbonate, which usually is remarkably pure. This, naturally, is adaptable for cement manufacture. However, if a magnesian limestone has been used, the magnesia may be too high for Portland cement. In some large alkali works, the amount of this waste product is so great that it has been used for cement. A similar waste product results from the extraction of magnesia from dolomite but nowhere is the supply large enough to be of any commercial significance for cement manufacture.

#### BLAST-FURNACE SLAG

Blast-furnace slag can be substituted for some of the ingredients that are used in the manufacture of Portland cement, and by its use true Portland cement can be produced of the same character as that made

from natural rocks. As is well known, blast-furnace slag consists of the major portion of the gangue of the iron ore and the limestone that has been added for a flux, together with some impurities of the coke. The gangue residue is mainly composed of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and the flux residue  $\text{CaO}$  and such impurities as it may have had. There is also some iron present. By adding more limestone, it is possible to obtain a mix that when burned will result in the standard Portland cement. Where high-magnesia limestones have been used for flux the slag is obviously unfit for Portland cement.

Slag Portland cement is generally cheap, as a waste product is utilized. If the slag is granulated in water as it emerges from the blast furnace the grinding cost is comparatively low but if it is cooled slowly in the air it forms a hard mass, which is much more difficult to grind.

#### NONCALCAREOUS MATERIALS USED IN CEMENT MANUFACTURE

Table 2 gives a list of materials that are sources of the necessary ingredients of cement. Certain of these substances are described elsewhere in this volume. The impurities of the limestones, particularly the argillaceous limestones, may suffice for all the necessary  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , as well as  $\text{Fe}_2\text{O}_3$ . Occasionally, however, raw materials composed more largely of these substances must be added to the limestones. Clays and shales are by far the most common. Slates by composition are similar but because they are harder and grinding costs are increased, they are seldom used. Sand and sandstones are used in some instances to obtain the proper silica ratio, although it is preferable to have the silica added in the form of aluminum silicates instead of quartz. When high-iron or high-aluminum cements are desired, ordinary iron ore or bauxite is employed.

#### RAW MATERIALS OF CEMENT

##### DISTRIBUTION AND POLITICAL AND COMMERCIAL CONTROL

The materials necessary for the manufacture of cement are worldwide in their distribution. In some places the best quality of stone is lacking or in areas of crystalline rocks suitable stone may be entirely wanting. These conditions are unusual for wide areas. A U. S. Government map of 1932 shows cement plants in all but the following 13 states: Arizona, Connecticut, Delaware, Massachusetts, Mississippi, Nevada, New Mexico, New Hampshire, North Carolina, North Dakota, Rhode Island, South Carolina and Vermont. Absence of plants is mainly due to scant population and hence poor market demand or to the proximity of cement plants in other states.

A somewhat similar situation prevails in the other countries of the world. When the domestic markets warrant, a search for materials is made, and usually with success. Increase in population and advance-

ments in industry are responsible for the building of new plants. The South American, Asiatic and African countries are less well supplied with cement plants than Europe and North America, as their industrial needs are smaller.

There is little political or commercial control over the raw products of cement. Rarely are they shipped far, and less rarely do they cross political boundaries. Tariffs have been placed on the finished cement in order to exclude competition with countries where labor and other costs are less. The United States Congress levied a duty on foreign cement, yet some European cement still comes into our Atlantic ports.

TABLE 7.—*Production and Price of Cement, 1926-1935*

Year	World Production, Bbl.	United States			
		Portland Cement		Natural and Puzzolan Cements	
		Barrels	Average Factory Price per Barrel	Barrels	Average Factory Price per Barrel
1926	365,869,787	166,635,061	\$1.71	2,104,891	\$1.39
1927	397,531,595	173,206,513	1.62	2,123,868	1.33
1928	423,330,106	176,298,846	1.57	2,210,404	1.31
1929	437,716,223	170,646,036	1.48	2,209,465	1.37
1930	413,948,830	161,197,228	1.44	1,792,083	1.38
1931	355,902,181	125,429,071	1.11	1,241,803	1.32
1932	283,197,287	76,740,945	1.01	456,785	1.35
1933		63,473,189	1.31	466,632	1.43
1934		77,747,765	1.54	671,588	1.42
1935		76,751,419	1.51	1,006,064	1.42

### PROSPECTING AND EXPLORATION<sup>12</sup>

In prospecting and evaluating cement-rock property it is first necessary to find suitable rock and then search out the adverse and favorable conditions. One of the serious problems confronting some of the cement companies is the presence of objectionable amounts of magnesia. It so happens that along the northern Atlantic border, where the bulk of the Portland cement of the country is consumed, there is much magnesia in the limestones, so that care must be taken in locating sites for cement plants. Some great thicknesses of limestones, aggregating hundreds of feet, contain no beds low in magnesia. Other localities contain interbedded high-magnesia and low-magnesia limestones, and in such places it must be determined whether it is possible to quarry or mine the desirable stone commercially without detrimental contamination from the high-magnesia beds. The problem is, therefore, first to determine the thickness and the chemical composition of all the beds.

In the early days of the industry, when all the stone in the quarry was hand-loaded, it was possible to sort the rocks shot down by the large

blasts, as it is relatively easy to train the quarrymen to distinguish between high-magnesia and low-magnesia. At present hand loading is not practicable.

If the usable material is in a band or bands 15 to 20 ft. thick with the beds either horizontal or vertical, the deposit may be workable, whereas inclined beds may so increase the cost of quarrying the good stone as to make the proposition unprofitable.

In the examination of a region of interbedded high-magnesia and low-magnesia limestones a distinction must be made between the ordinary averages of chemical composition and the weighted averages. If all the beds were of equal thickness, averages would be alike. In the bed described in Table 8 the distinction is well brought out. Of course, it must be known how the sampling is done. Some prefer to have all the composite samples represent equal measured distances. The writer believes that a better picture of the exact situation can be obtained by sampling separately each bed regardless of the varying thicknesses.

TABLE 8.—*A Typical Limestone Bed*

Thickness, Ft.	CaO, Per Cent	MgO, Per Cent
10	33.42	16.66
2	42.66	2.46
8	29.10	15.93
3	48.22	1.27
Arithmetical average.....	38.35	9.08
10 ft. × 33.42 CaO = 330.42	10 ft. × 16.66 MgO = 166.60	
2 ft. × 42.66 CaO = 85.32	2 ft. × 2.46 MgO = 4.92	
8 ft. × 29.10 CaO = 232.80	8 ft. × 15.93 MgO = 127.44	
3 ft. × 48.22 CaO = 144.66	3 ft. × 1.27 MgO = 3.81	
23 793.20	23 302.77	
Weighted average (793.20 ÷ 23)..... 34.49 CaO	Weighted average (302.77 ÷ 23)..... 13.16 MgO	

In sampling thick beds it is necessary to take pains to secure fairly uniform amounts from all parts of the bed, since changes in chemical composition in different parts may not be noticeable in the appearance of the stone. These might be observed on weathered surfaces but obviously it is important to have the samples taken from fresh stone.

Having recognized the presence of useful and useless interbedded limestones in a property designed to furnish the stone for manufacture of Portland cement, it next becomes necessary to determine its real value if the outcrops do not furnish sufficient information. This can be done



either by trenching or by drilling. Naturally, the method chosen should be the cheapest, provided it will furnish the needed information.

Where the overburden is thin and the strata dip gently, trenching to expose the different beds is satisfactory. If certain of the beds are overlain by upwards of 10 ft. of overburden, it may not be economical to use this method. In addition, the edges of the beds exposed in the trenches may be so weathered that samples obtained for analysis may give misleading results. It is not unusual to find beneath a soil cover limestones altered by differential or selective solution to a depth of 6 to 8 ft. and locally even more. The alteration is mainly in the partial solution of the  $\text{CaCO}_3$ , but other chemical changes may be produced. Where the strata are horizontal or approximately so, trenching cannot be employed except along hillsides, where the beds outcrop, and there only when the hillside debris or talus is not too deep.

In prospecting limestones by drilling various conditions must determine whether the ordinary well drill or a core drill is to be employed. In some places, particularly where the strata are horizontal, either one can be used. In such cases there is sometimes a difference of opinion as to which is preferable. Under almost all conditions the well-drill method is much cheaper and should be chosen if the results are satisfactory. If the core drill could be relied upon to furnish 100 per cent of core, there would be no question of its superiority, but when the beds are shattered, cavernous, partly decomposed, or of varying hardness, the core recovery may be even less than 50 per cent. The percentage of recovery depends at times upon the skill of the drill operator. By running the drill more slowly and removing the core at short intervals better results can usually be obtained. When the core recovery is disappointing, the writer has insisted upon the collection of the cuttings from the sludge overflow by means of a screen attached to the top of the casing and an analysis of this material as well as of the cores.

In certain hard and fairly uniform rocks lying in a horizontal position, prospecting limestone by well drills will give reliable results. In other places, particularly where there is clay mixed with the cuttings and washing is necessary, the results may be largely in error. If certain strata are unusually soft, they may be so finely pulverized as to have most of the material washed out with the clay. At times washed samples actually show less  $\text{CaCO}_3$  in the analysis than the unwashed, even though there is considerable clay present. In well-drill prospecting there is also danger of pieces of the rock from higher levels falling to the bottom of the hole and becoming mixed with the samples from the lower strata. Further, a sample representing only a small part of the cuttings may not be truly representative of the interval drilled.

In regions of horizontal strata the best plan in many cases is to prospect most of the property by the cheaper well-drill method, and to check

by means of a few core-drill holes. Where the strata are vertical, or nearly so, naturally the well drill, capable of drilling only vertical holes, is not applicable, nor should core-drill holes be put down vertically, as in either case a thickness of rock only the diameter of the hole is proved. Under conditions of steeply dipping or vertical beds the character of the strata can be obtained only by inclined holes. If the holes can be driven at right angles to the bedding planes, the maximum number of beds will be penetrated, and that means the maximum amount of useful information with the minimum amount of drilling. Where the surface is flat and the beds dip steeply, it is generally advisable to drill the holes at an angle of about  $30^{\circ}$ , less if the rocks are fresh just beneath the soil cover, or at a steeper angle if there is a considerable depth of decomposed rock. There are two reasons for doing this. First, it is generally regarded as better not to extend the holes to a vertical depth much greater than the proposed quarry depth, simply because the information sought concerns only the stone that will eventually be quarried. Accordingly, the angle should not be too steep. The objection to having the hole only slightly inclined is that much of its length will be close to the surface and rather largely in stone that may have been affected by surface weathering.

In starting a new diamond-drill hole it is advisable to locate it so that a few feet of strata previously cut at depth will also be sampled in the beginning of the next hole. This is desirable as a check in certain cases, and in others is useful because the first few feet of hole pass through decomposed stone not representative of the same beds in depth.

The prospecting of strata either greatly folded or faulted is difficult. Perhaps some particular bed may be recognized, if it is cut more than once in the same hole, but in limestones it is seldom possible definitely to recognize individual beds in the core samples when they are cut more than once. By noting the angle at which the strata are cut throughout the entire hole and later comparing the results with the data from other holes, the true structure may be worked out. It generally requires both skill and patience. If the underground structure is complexly folded it becomes impossible to decipher the character of the folding from the cores, and the average composition of the entire holes must be considered in reaching an opinion as to whether the stone is desirable or otherwise. If the results show that it is on the margin of usefulness, it is extremely risky to plan to open a quarry unless the amount of drilling done is excessive by having holes spaced at very close intervals.

After results have been obtained there are many methods for recording them. Many graphic methods have been used for presenting as accurate a picture as possible and in a way by which the essential points can be easily grasped. Geological training and experience, plus common sense and a keen appreciation of the economics of the industry, are the requisites in any person prospecting a cement property.

## MINING METHODS

The quarry and mining methods employed by the cement companies have been thoroughly discussed by Bowles<sup>1</sup> and Thoenen,<sup>16</sup> so that it does not seem advisable to go fully into that subject. Naturally, the object in obtaining rock for cement manufacture is to get as clean and uniform a product as possible at the lowest cost. This is accomplished in the great majority of places by open quarrying. The character, shape and size of the quarry naturally depends on the thickness, uniformity and structure of the rock.

Generally there is a layer of thick or thin residual clay overlying the usable rock, which always must be removed in order to obtain a proper mix. In places where the rock is apt to be deficient in lime, an additional thickness of rotten rock in which much of the  $\text{CaCO}_3$  has been removed in solution must also be removed. Deep pockets of residual clay are also present in places, which can be excavated only by hand pick and shovel.

Where the limestone is obtained from open quarry it is customary to develop a rounded or half-circle face, so that materials may be obtained from several points at the same time and differences in composition averaged. As a quarry is deepened it finally attains a depth at which it is advisable to work it in benches instead of a single high face. Churn drills are commonly used for the drilling of the holes for blasting. The spacing of the holes from each other and from the face of the quarry varies according to the rock. A fair average is probably 15 ft. When the size of the quarry permits, a number of holes are shot at the same time. If some of the stone is thrown down in large blocks in the primary blasting, there must be considerable secondary blasting done to reduce the size sufficiently for loading.

Steam or electric power shovels have almost completely replaced hand loading in the quarry. The rock is generally taken out of the quarry in cars by cable but in some places trucks are employed.

Where the overburden of waste material is excessive or the workable beds are thin and steeply dipping, it is necessary to substitute underground mining for surface quarrying. A number of cement companies obtain all of their stone from mines. The methods employed are similar to those of coal mining except that the rock pillars are stronger and generally little or no timbering is required. A cleaner product can be obtained than in surface quarrying. Under most conditions the costs are greater, so that little limestone mining is done except when quarrying costs become excessive.

BENEFICIATION OF LIMESTONE FOR CEMENT MANUFACTURE<sup>10</sup>

Until recently cement manufacturers have been concerned only with the chemical composition of limestone and have completely ignored the mineralogical constitution. The fitness or unfitness of particular stones

has been determined by the chemist. Little consideration has been given to the removal of objectionable portions or to the rectification of improper ratios of the constituents except by mixing with other rocks of different composition.

The minerals of which limestones are composed have unlike physical properties and behave differently when the rocks are crushed. Calcite and dolomite, because of their excellent cleavage, are readily broken into fine rhombs; the mica is separated into thin flakes; the quartz without cleavage planes is less easily broken and the fragments are irregular in shape; and the minor minerals behave likewise in definite and distinctive manner. Some investigators therefore considered it possible to make some separation of the mineral constituents by grinding, screening or tabling. Experiments proved the feasibility of such a procedure for

improving the grade to such a slight extent as to be of little value in commercial operations. Separations based on specific gravity have been suggested but are difficult because of the slight differences between quartz, calcite and dolomite. The conclusions concerning the practicability of these methods have been negative.

With the extension of froth flotation into the field of the non-metals, experimentation on limestones was suggested. Some people considered the expense

prohibitive, but as the result of a long series of experiments a commercial flotation plant was put in operation by the Valley Forge Cement Co., West Conshohocken, Pa., on March 15, 1934. It has been so successful that plans have been made by cement companies in Argentina, South Africa, France and Finland to erect similar flotation units for the beneficiation of their raw limestones. A rather wide variety of limestones has been used in the investigations and with success in each case, although each type of stone presents distinctive problems that demand changes in the procedure. There is no doubt that within a few years many, perhaps most, cement companies will process their limestones before the latter are fed into the kilns.

In the froth flotation of limestone the object thus far has been to remove only portions of certain minerals in order to obtain the requisite ratios for a mix without the addition of other stone. Usually this means a lowering of the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  with reference to the  $\text{CaCO}_3$ . It is possible to separate the quartz grains, thus lowering the silica

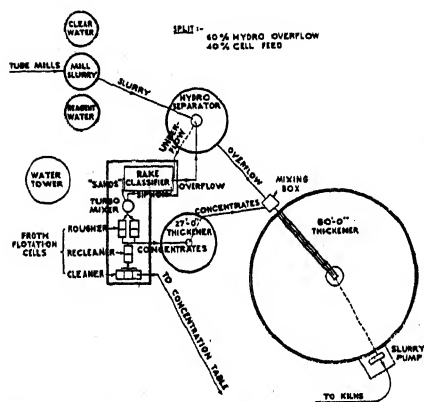


FIG. 1.—FLOWSHEET OF FLOTATION PLANT, VALLEY FORGE CEMENT CO.<sup>10</sup>

content, or remove part of the mica and thereby lower both the  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . The rectification may mean only a change of a few per cent or, as in one case now under consideration, it may involve an increase of  $\text{CaCO}_3$  from 40 to 75 per cent.

Each type of limestone calls for individual experimentation before the plant is planned, and, further, any flotation installation must be sufficiently flexible to meet the changing composition of the quarry rock coming into the mill. For this reason each flowsheet has its own char-

PURE CONSTITUENTS IN TONS BASED ON 700 TONS OF MILL STREAM PER 24 HOURS

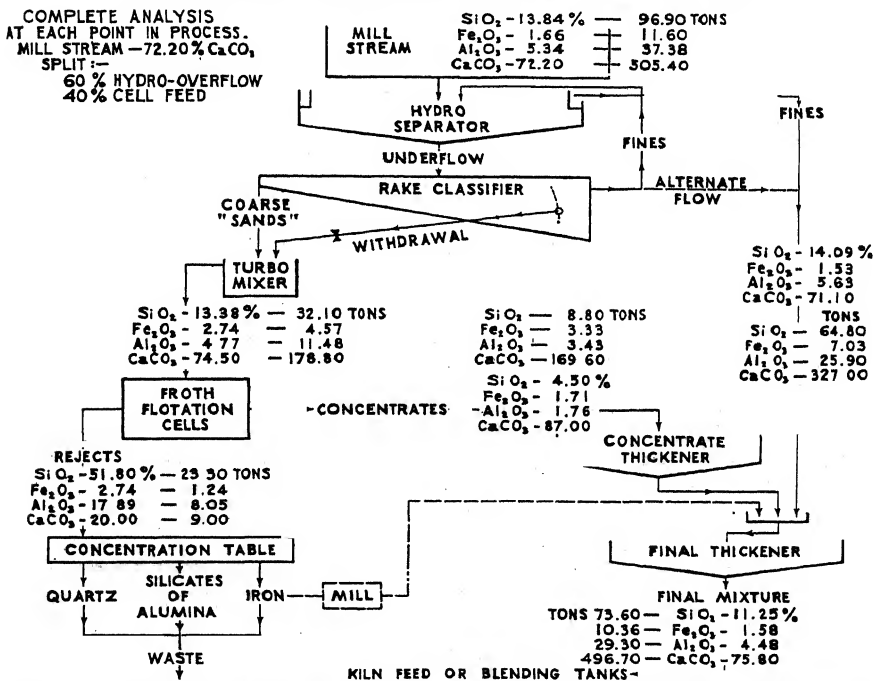


FIG. 2.—FLOWSHEET OF VALLEY FORGE CEMENT CO. SHOWING RESULTS OF ACTUAL OPERATIONS.<sup>10</sup>

acteristic features. Some of these are much more elaborate than the one now in operation by the Valley Forge Cement Co. but inasmuch as they have been developed in the laboratory alone up to the present time it seems inadvisable to include descriptions of them in this article. The two flowsheets presented (Figs. 1 and 2) illustrate the process and the analysis of the material at different stages. The concentration table has not been installed. The rock is ground fine enough for 85 per cent to pass through a 200-mesh screen. Oleic acid is used as a collecting agent and cresylic acid or B-23 alcohol to produce the frothing. The amount of stone passed through the flotation cells varies with the grade of the stone. If the mill feed is low in  $\text{CaCO}_3$ , a larger amount is withdrawn from the rake classifier and treated in the cells.

The principal advantages of limestone processing are summarized as: (1) reducing quarry costs in that poor stone when encountered need not be wasted, (2) otherwise useless stone situated near plant can be made useful, (3) grinding costs are reduced by elimination of the larger quartz particles, (4) fuel consumption is decreased by the discarding of some of the coarse quartz, (5) the quality of the cement is improved by making better ratios possible. These and other minor advantages in actual practice have been found to more than offset the cost of beneficiation.

Froth flotation in the beneficiation of limestone for cement is still so recent that it is difficult to predict the future. It may revolutionize the utilization of limestone for many purposes and develop in importance comparable to its position in the metallic products.

In the manufacture of high-alumina cement, bauxite is used. White clay is the additional ingredient used in the manufacture of white cement. For the production of dark colored cements and for cements that produce a minimum of heat in setting, several varieties of iron ore have been used.

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## CHALK\*

BY HEWITT WILSON†

**C**HALK is soft limestone formed from calcareous remains of microscopic organisms. Whiting is the finely divided product obtained from limestone rocks of which the chief constituent is calcium carbonate. Until recently most whiting was made from European chalk, but ground limestone, marble, and precipitated calcium carbonate have replaced a large amount of foreign chalk on the American market.

## DISTRIBUTION, ORIGIN AND MODE OF OCCURRENCE

*European Chalk.*—The present outcrops of Cretaceous chalk are found in the area between Antrim, Ireland, and Uralsk, East Prussia, and from the northern deposits in Sweden and Scotland to the southern exposures near Nice in southern France. The present supply of commercial chalk and whiting is taken from the chalk cliffs between Dover and Hull, England, from near Mons, in the Departments of Pas de Calais and Nord in northern France, and also from Denmark and Belgium.

*United States.*—Some grade of limestone is found in every state of the Union, but the true chalk of Cretaceous age is limited to the Central and Southern States. Niobrara (Cretaceous) chalk outcrops are found as a narrow band encircling the Black Hills, in South Dakota, Wyoming, and Nebraska, and in much larger exposures in southeastern South Dakota, eastern Nebraska and western Kansas. A chalk band extends from west central Arkansas into Oklahoma and connects with the Austin beds, which outcrop on a northeast-southwest band extending almost across Texas. In the Southeastern States the Selma chalk extends from western Tennessee through northwestern Mississippi and across central Alabama. Some of the soft, creamy colored limestones of northern

\* Based on an investigation made by the U. S. Bureau of Mines at its Northwest Experiment Station, Seattle, Wash., in cooperation with the College of Mines, University of Washington. Published by permission of the Director, U. S. Bureau of Mines.

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Florida, Georgia, Alabama, and probably Mississippi, Louisiana, and South Carolina, are similar to chalk in original hardness, fineness of grain, and working properties, but have a different origin.

*Origin.*—Although the remains of echinoids, mollusks, corals, sponges, and even vertebrate animals are included as fossils in chalk deposits, and are of primary importance in faunal and stratigraphic studies, they are secondary in importance to the microskeletons of coccolithophores and rhabdoliths that constitute the larger part of the chalk. These are plant organisms that secrete a number of calcareous (coccoliths) or trumpet-shaped bodies (rhabdoliths) on their surfaces, and on dying their calcareous remains mingle with precipitated calcium carbonate and the remains of foraminifera and other organisms that form an important part of deep-sea deposits.

### COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

*Commercial Control.*—European chalks have had an advantage in the domestic market because of their light colors, plasticity, fineness of grain, ease of preparation by simple grinding and classification, and comparatively cheap transportation (by water). With the exception of a few American chalks from Arkansas and Kansas, from which putty has been made, domestic chalks have been used on an extensive scale only for Portland cement. The domestic chalks have the fineness of grain of European chalks, a similar paleontological origin, and an even stronger putty plasticity, but a recent study<sup>19</sup> indicated that the domestic materials did not equal the European in color and purity. Their chief value is for colored fillers and as plasticizers for the less plastic powdered limestones and marbles. Their occurrence is so widespread that undoubtedly better colored deposits will be found in the future.

Certain limestones of Illinois, Missouri and Pennsylvania develop good plasticity with the proper grinding treatment, and some of these have better color than the European chalks. The fortification of weakly plastic limestones and marbles with European chalks undoubtedly will continue for some time, especially along the Atlantic and Pacific coasts. These districts likewise may use ground shell as a plasticizer if a sufficient tonnage can be secured cheaply.

Some of the golden brown chalks of South Dakota, Kansas, Arkansas and Texas have colors similar to ochers and siennas and when diluted produce creams of more desirable hues than the gray-putty colors of the European chalks. The darkest of the Alabama chalks give a "driftwood" gray pigment on dilution.

The purest white calcium carbonate products can be made by grinding the white marbles from Georgia, Vermont, Alabama, California, and other states. These are far whiter than the European chalks but are of low

<sup>19</sup> References are at the end of the chapter.



plasticity. Limestones and marbles as a source of calcium carbonate for precipitated whiting are more accessible to the eastern markets than are the domestic chalks found in the Central and Southern States.

The 1934 tariff rate for whiting or Paris white, dry, ground or bolted, is  $\frac{4}{10}$  of a cent per pound. Whiting ground in oil (putty) has a duty of  $\frac{3}{4}$  of a cent per pound. Crude chalk is duty free, while manufactured chalk products and precipitated chalk have a duty of 25 per cent ad valorem.

*Production and Consumption.*—Fig. 1 shows the quantities and values of imported whiting and products for the period 1920 to 1934 in compari-

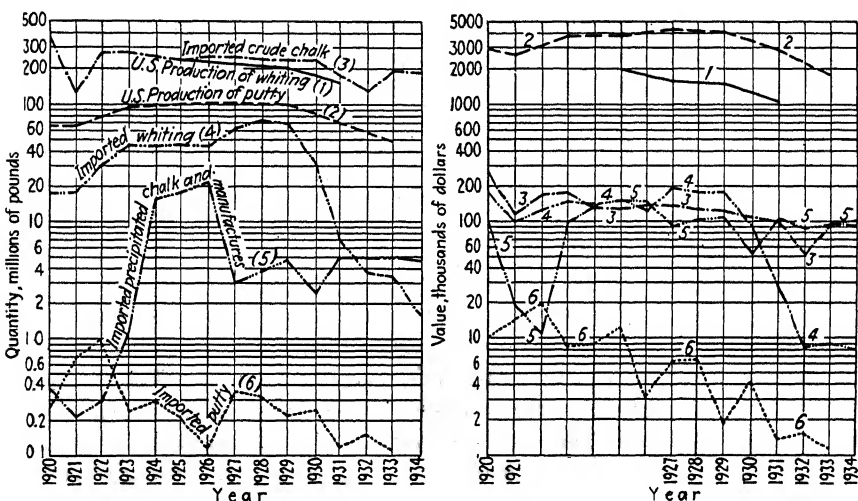


FIG. 1.—IMPORTS AND PRODUCTION OF CHALK AND WHITING FOR THE UNITED STATES, 1920 TO 1934.

Domestic production figures from the U. S. Bureau of Census, and import figures from Foreign Commerce and Navigation of the United States, U. S. Bureau of Foreign and Domestic Commerce. The production data are incomplete.

son with the total domestic production of whiting and putty. Imports of crude chalk and precipitated whiting have maintained a comparatively higher level since 1929 than importations of ground whiting and putty. It is not known how much of the domestic production was made from imported crude chalk.

## PROSPECTING, EXPLORATION, MINING AND PREPARATION

*Prospecting, Exploration and Mining.*—The identification of the hard limestone rock is one of the simplest in the field because of its moderate hardness and effervescence with weak acids. However, the hardness test of calcite is lost in dealing with the softer chalks and marls and many impurities minimize the value of the effervescence test. Hence the purity of the sample and the character of the impurities must be deter-

mined by chemical analysis and petrographic studies. Core or churn drilling, prospect adits, or shafts are necessary to determine the extent and uniformity of the deposit unless these properties are indicated by satisfactory exposures. Freedom from grit is an important property in whiting and therefore quartz and other hard impurities must be determined. The removal of a stained overburden in advance of quarrying is very important in securing a white limestone for whiting. Limestone is obtained chiefly from open-pit quarries in which deep-hole blasting and power-shovel loading are employed.<sup>2</sup> The average mining cost, according to Thoenen,<sup>16</sup> for 30 of the open-pit limestone quarries in the United States was 67¢ per ton, but if the overburden is too heavy or the surface deposits are exhausted underground mining must be employed and the cost rises to about 96¢ per ton. Limestone is too low in price to justify mine timbering, and underground methods are used only where the rock is strong and sound enough to maintain roofs in drifts and rooms. Most of the 64 underground limestone mines in the United States studied by Thoenen<sup>16</sup> were of the adit or tunnel type, a few having vertical or inclined shafts. The single-breast stope was common for thin flat beds, and bench methods were used for thicker beds with the room-and-pillar system or its modifications.

*Ground Whiting.*—Chalk whiting made by the older English method is water-ground in edge-runner or stone-drag mills, after the flint pebbles have been removed by hand. The milky suspension is classified by water settlement in a series of tanks, producing waste sand and coarse particles in the first tank, "commercial," "gilders," "extra gilders," and "Paris white" in the following settling basins. Dewatering is accomplished by siphoning the clear water from the chalk sludge, filter-pressing and drying. The dried product is pulverized, sieved, and packed. Modern equipment for wet-ground whiting includes the use of rolls, Mueller grinders, and pebble mills for grinding; bowl and cone classifiers and hydroseparators for classification; and thickeners, continuous filters, and rotary driers for dewatering. In the cheaper dry process the crushed rock is dried in a rotary drier, coarse-ground in rolls or swing-hammer mills, and finely ground in impact pulverizers, roller mills, ball mills, or air-swept tube mills, often in closed circuit with mechanical pneumatic separators, which produce a product satisfactory for many whiting purposes. Quartz or porcelain-lined mills and flint pebbles are necessary for grinding the low-iron ceramic whiting.

*Precipitated Whiting.*—Quicklime, obtained by calcining limestone, is slaked to the hydroxide or milk of lime suspension, which is then treated with carbon dioxide gas produced by burning coke. The gas is scrubbed as it enters the upright recarbonation cylinders (each 6 by 18 ft.). The completion of the reaction is determined by phenolphthalein or other indicators and from 2 to 3 hr. is required for the reaction. The pre-

cipitated calcium carbonate is dewatered in filter presses and the dried filter cakes are pulverized for packing.

Precipitated calcium carbonate is obtained also as a by-product from the manufacture of caustic soda in paper mills:  $\text{CaO} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NaOH}$ . This product may contain traces of alkali, which restricts its use. Calcium carbonate is produced by other industrial chemical processes, including the manufacture of basic magnesium carbonate from dolomite. Certain "precipitated" grades apparently are not chemically precipitated but are merely finely ground and water-settled or precipitated from suspension, not solution.

Several manufacturers are now adding small amounts of fatty acids and their derivatives to limestone during fine grinding, to increase the plasticity, the mobility in the dry state, and the waterproofing and coagulation properties.

### TESTS AND SPECIFICATIONS

Chemical analysis indicates the purity of the whiting, the character of the impurities, something of the color, especially the color that can be expected after ignition, and differentiates between the calcic and dolomitic varieties of limestone. The chemical requirements are particularly important in the chemical and ceramic industries, where a high content of calcium carbonate is required and the impurities, especially iron oxide, are not wanted. Class 1, ceramic whiting, is limited to a minimum of 96 per cent  $\text{CaCO}_3$ , a maximum of 1 per cent  $\text{MgCO}_3$ , 0.25 per cent  $\text{Fe}_2\text{O}_3$ , 2.0 per cent  $\text{SiO}_2$ , and 0.1 per cent  $\text{SO}_3$ . Class 2 permits 8 per cent  $\text{MgCO}_3$ .<sup>23</sup> The physical properties, such as fineness, color, working ability, time of settling, etc., which are the essentials for most fillers, bear little relation to the chemical composition, even though specifications may be based upon the chemical analyses of satisfactory whittings.

The physical requirements are more important than chemical composition in the paint industry, since such a wide variety of white and colored nonmetallic fillers, differing markedly in composition, are used in paints. The rubber industry limits its specifications to nearly pure calcium carbonate, which from the chemical basis can be supplied by many domestic marbles, limestones and precipitated whittings. However, fineness, strength, and workability are thought to be more important. The putty trade is interested in plasticity, oil absorption, oil retention and fineness.

Alkalinity is important in dentrifice, toilet and chemical products, and the curing of rubber is affected by variations in alkalinity. However, pure calcium carbonate is slightly soluble in water and the pH value of whiting is greater than 7.8. Both the Federal Government and the American Society for Testing Materials have titration methods

for determining alkalinity of whittings, but there is a need for research and correlation of these tests to specific service. A recent study<sup>19</sup> indicated that the precipitated whittings were highly alkaline (pH of 8.3 to over 9.6), which may cause a saponification of the linseed oil used in putty and paint.

Fineness specifications are limited to a restriction of those particle sizes coarser than 325 mesh. This is a satisfactory limitation of the coarse-grit content but is inadequate as an indicator of the other properties. Settling and sedimentation tests,<sup>17,18</sup> air separators,<sup>14</sup> and microscopic examination methods,<sup>7</sup> have been used in research laboratories for more accurate particle-size measurements of grains less than 50 microns in diameter.

The important properties required for manufacture of putty are: (1) plasticity, (2) hardening ability, (3) low oil absorption, (4) color, (5) chemical inertness, (6) insolubility in water, (7) resistance to "bleeding" oil, and (8) permanence. The best method of testing properties 1, 2, 7 and 8 is a simulative service test on the putty samples for several months, arranged by an experienced operator.

Although whiting cannot compete with white lead, zinc oxide, and other opacifiers, because of its low refractive index, it is used as an extender, body material or filler in oil paints. The depth of a suspension through which a given object or line can be distinguished under controlled conditions is used as a relative measurement of opacity.

Other tests of whiting include the settling rate in oil, the bulk density of the "fluffed" whiting to represent the freshly bagged product (4.4 to 10.0 grams per cubic inch), the volume loss (30 to 47 per cent) of the dry powder on packing and shaking, and the water-flow test to indicate the minimum amount of water required to make a flowing paste.

#### USES, MARKETING AND PRICE

The important uses include fillers or extenders in calcimine or cold-water paints, oil paints, putty, rubber, oilcloth, linoleum, window shades, cigarette papers, white ink, white shoe dressing, picture-frame moldings, dolls, dyes, tooth paste, fireworks, wire insulation, neutralizing agents in fermentation and general chemical processes, medicines and explosives. The paint industry is reported to use about 50 per cent of the imported whiting, the rubber industry about 35 per cent, and the putty trade about 10 per cent.

In many industries the chalk whiting is still preferred, especially the water-ground chalk and overground limestone and marble, and large quantities of duty-free, crude chalk are shipped to this country for domestic preparation along the ocean fronts where ocean freight rates from Europe have an advantage over rail rates from interior points. However, the use of better grinding equipment, control, and

more careful selection of raw material is giving the American producer a chance to establish his product in this country, especially in the Middle West.

After the high prices following the war, commercial chalk whiting remained at 1.0¢ per pound from 1922 to 1932, then dropped to 0.56¢ in 1934. It was quoted at 0.6¢ in the May 11, 1936, issue of the *Oil, Paint and Drug Reporter*. Gilders bolted chalk whiting ranged from 1.2 to 1.4 times that of the commercial grade. Gilders extra bolted and Paris white ranged from 1.2 up to 1.5 times the commercial grade, their present prices being 0.75¢. Prices for dry-ground commercial limestone, reported only since 1930, have remained at 0.5¢ for the product 99.75 per cent finer than 300 mesh (\$2 freight allowed). The present price of the wet-ground limestone is 0.575¢, the putty grind is 0.75¢, and the "precipitated" grade of ground limestone is 0.75¢ per pound. Chemically precipitated chalk in the five grades, extra light, light, medium, heavy and extra heavy, is priced at 3.0 and 5.0¢ per pound.

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## CHROMITE

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**T**HERE are many varieties of the chrome ore known as chromite, only one of which is of commercial importance. In its pure state this ore consists of ferrous chromite,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ . The commercial ores do not contain pure ferrous chromite, but consist of minerals derived from it, together with varying amounts of impurities.

Mineralogically, commercial chrome ores are composed of two definite and distinct components. The first, or primary component, is called chromite, and chemically this component is ferrous chromite in which a portion of the ferrous oxide ( $\text{FeO}$ ) has been replaced by magnesium oxide ( $\text{MgO}$ ), and a portion of the chromic oxide ( $\text{Cr}_2\text{O}_3$ ) has been replaced by alumina ( $\text{Al}_2\text{O}_3$ ). In other words, the primary component is a chemical entity, in which the molecular sum of the  $\text{FeO}$  and the  $\text{MgO}$  equals the molecular sum of the  $\text{Cr}_2\text{O}_3$  and the  $\text{Al}_2\text{O}_3$ . The secondary component of chrome ores, the impurities from a mineralogical viewpoint, consists of impure magnesium silicates. The impurities in the magnesium silicates may be various iron compounds, brucite, and aluminum silicate. The following magnesium silicates have been found as the secondary components of various chrome ores: clinoenstatite ( $\text{MgO} \cdot \text{SiO}_2$ ); enstatite ( $\text{MgO} \cdot \text{SiO}_2$ ); forsterite ( $2\text{MgO} \cdot \text{SiO}_2$ ); parasepiolite ( $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ); chrysotile ( $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ); antigorite ( $3\text{MgO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ); talc ( $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ ); hypersthene ( $(\text{MgO}, \text{FeO}) \cdot \text{SiO}_2$ ); serpentine ( $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ); sepiolite ( $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ). The chemical analyses of the chromites vary, of course, with the amounts of  $\text{FeO}$  and  $\text{Cr}_2\text{O}_3$  replaced by  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  respectively. The analyses of the ores produced in one locality are peculiar to that locality and analytical data on the various ores will be given later.

## PROPERTIES

The color of chromite is red to black, sometimes yellowish red in thin sections; streak, brown. The hardness is 5.5; specific gravity, 4 to 4.6. Luster is submetallic to metallic. Sometimes it is feebly magnetic.

The softening point of chromite is a function of the secondary component and varies from  $2300^\circ$  to  $2600^\circ$  F., although the mineral itself is

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classified as infusible. Chromite is one of the very few iron oxide compounds that cannot be reduced by CO. It is neutral and almost insoluble in slags and fluxes. Its reactivity increases directly with the percentage of iron present in the primary component. Its refractory properties

TABLE 1.—*Production of Chromite<sup>a</sup>*

Country	Crude Chromite, 1931-1935, Metric Tons					Percent- ages of Total World Pro- duction Based on Annual Average for the Years 1932-1934, Inclusive
	1931	1932	1933	1934	1935	
Australia.....	61	99	905	1,744	605	
Brazil.....					5 <sup>b</sup>	
Bulgaria.....				85	<sup>d</sup>	
Canada (shipments).....		71	27	101	1,038	
Cuba.....	15,197 <sup>c</sup>		24,154 <sup>c</sup>	50,162 <sup>c</sup>	48,509 <sup>c</sup>	5.59
Cyprus (shipments).....	203	1,000		982	1,198	
Greece.....	5,634	1,555	14,784	30,694	31,984 <sup>b</sup>	
Guatemala.....	92 <sup>c</sup>		2,094 <sup>c</sup>	805 <sup>c</sup>		
India (British).....	20,233	18,152	15,775	21,922	<sup>d</sup>	4.20
Indochina.....	2,800				<sup>d</sup>	
Japan.....	9,675	12,492	19,897	27,222	<sup>d</sup>	4.48
New Caledonia.....	74,150	69,492	50,072	55,182	<sup>d</sup>	13.14
Norway.....		409	326	42	<sup>d</sup>	
Philippine Islands.....					21,292	
Rumania.....			29		<sup>d</sup>	
Southern Rhodesia.....	81,623	15,692	35,046	72,099	105,834	9.24
Turkey (Asia).....	55,216	55,196	75,379	119,844	150,504	18.84
South Africa.....	23,335	19,371	34,078	61,357	90,431	8.63
Russia.....	67,000 <sup>c</sup>	68,000 <sup>c</sup>	112,728 <sup>c</sup>	129,200 <sup>c</sup>	<sup>d</sup>	23.32
United States (shipments).....	272	157	857	375	523	
Yugoslavia.....	58,384	43,925	26,248	47,352	60,000	8.84
Others.....						3.72
	414,000	306,000	412,000	619,000		

<sup>a</sup> Minerals Yearbook, 1936, U. S. Bureau of Mines.

<sup>b</sup> Exports.

<sup>c</sup> Imports into the United States. The figures for 1934 represent "imports for consumption"; those for prior years, "general imports."

<sup>d</sup> Data not available.

<sup>e</sup> Approximate production.

decrease as the iron increases. Pure ferrous chromite is not stable at high temperatures.

## GEOLOGY, DISTRIBUTION AND PRODUCTION

The ore, as it occurs, is granular, compact, or is disseminated in country rock, and on rare occasions is found in small octahedral crystals. It is always associated with serpentine minerals and most of its deleterious



properties, from the refractory viewpoint, can be attributed to the associated minerals. Chrome ore occurs in peridotite, or in the serpentine derived from it, almost entirely as magmatic segregations. Frequently residual deposits occur, as chrome ore is very resistant to atmospheric influences, and it is, therefore, very common in gravels. The deposits, in place, are usually lenses of irregular outline, varying in size but seldom exceeding a few thousand tons.

Chrome ore was first found in the United States near the boundary line between Pennsylvania and Maryland. Prior to the World War, Southern Rhodesia and New Caledonia were for some years the chief producers of chromite. Their productions were about equal and together they furnished 80 to 90 per cent of the world's supplies. Of the other producing countries, Turkey, Russia, Greece and India were the most important. During the war, owing to shortage of ocean transportation and other causes, production was greatly stimulated in the United States, Canada and India. Following the war, conditions reverted practically to their prewar status. Recently, however, Russia, Turkey and Cuba have become important factors in the world's production of chromite. Development of deposits in the Philippine Islands indicates that this locality may also become an important source of supply. Today the United States is one of the smallest producers of the ore, although it is by far the largest user. Table 1 shows the world's production of chromite in metric tons and in percentages.

The United States contains sections where large amounts of chrome ore are found. Probably the largest known are in California and Montana, although there is some chrome ore in Georgia, Maryland and Pennsylvania. During the last few years production in the United States has not exceeded a few hundred tons annually.

Table 2 shows the domestic sales, imports and apparent supply of chromite in the United States for the years 1931 to 1935; also the chromite imported into the United States by countries for the same years.

#### USES AND PREPARATION

In the United States 50 per cent of the consumption of chromite is for metallurgical purposes, 40 per cent for refractory purposes, and 10 per cent for chemical and other purposes.

The specifications on the chromites vary with the use. For metallurgical purposes, ores high in  $\text{Cr}_2\text{O}_3$  are usually selected. For chemical purposes, ores which are easily decomposed, that is, the high-iron ores, are usually preferred. For refractory purposes the percentage of  $\text{Cr}_2\text{O}_3$  in itself is not a decisive factor, and ores relatively low in chromic oxide content are used if the percentage of  $\text{Al}_2\text{O}_3$  is relatively high. The physical condition of the ore and the placement of the gangue are important factors in ores for refractory purposes.

The chrome ore used in the refractories industry is sometimes heat-treated to recrystallize the chromite, thus stabilizing it, decreasing its chemical activity and distributing the gangue minerals so that their deleterious effects are minimized. Chromite recrystallizes slowly at 2900° F. and rather rapidly at 3400° F. Chromite that is heat-treated beyond the point at which recrystallization takes place, but below its fusion point, yields the best product for refractory purposes. Sometimes

TABLE 2.—*Crude Chromite in the United States<sup>a</sup>*  
LONG TONS

Year	1931	1932	1933	1934	1935	1935 value
Sales from domestic mines...	268	155	843	369	515	
Imports (general).....	212,528	89,143	116,511	192,297	259,063	
Apparent available supply...	212,796	89,298	117,354	192,666	259,578	

IMPORTED INTO THE UNITED STATES

From						
Africa <sup>b</sup> .....	75,670	17,702	13,186	48,848	92,682	\$1,501,554
Belgium.....	482					
Brazil.....					2	26
Canada.....			49	30	2,888	62,941
Cuba.....	14,957		23,772	49,370	47,743	253,847
Greece.....	28,893	16,395	11,499	23,301	20,692	197,430
Guatemala.....	91		2,061	792		
✓India (British)...	8,664	7,857	4,152	400	14,926	155,870
Netherlands.....				259		
Oceania.....	39,579	11,550	15,150	19,530	55,686	1,041,957
Other Asia.....				1,100		
Philippine Islands					787	15,047
Turkey (Asia)....	2,198	17,602	27,854	28,730	16,060	267,294
Russia.....	17,736	4,800	13,261	19,937	3,412	53,721
United Kingdom.	24,258	13,237			4,185	54,804
Yugoslavia.....			5,527			
	212,528	89,143	116,511	192,297	259,063	3,604,491

<sup>a</sup> Minerals Yearbook, 1936, U. S. Bureau of Mines.

<sup>b</sup> Includes Southern Rhodesia and Union of South Africa.

the chrome ore is recrystallized by fusion, but in ore thus treated the segregation and distribution of the secondary component in the cooled mass are usually poorer from a refractories-manufacturing viewpoint than they were in the original ore.

Chromite is used commercially for the manufacture of metallurgical products, refractories used in metallurgical plants, for cements and plastics used in the construction of furnaces, and for the production of chemical products such as chromates and pigments.

Most chromite is mined from quarries or open pits, although there are some underground operations. The ore is usually shipped in the condition in which it is mined. However, there are concentration plants in Serbia, in Turkey, in Canada, and in California, from which shipments of concentrates for the manufacture of chemicals, refractories and alloys are made.

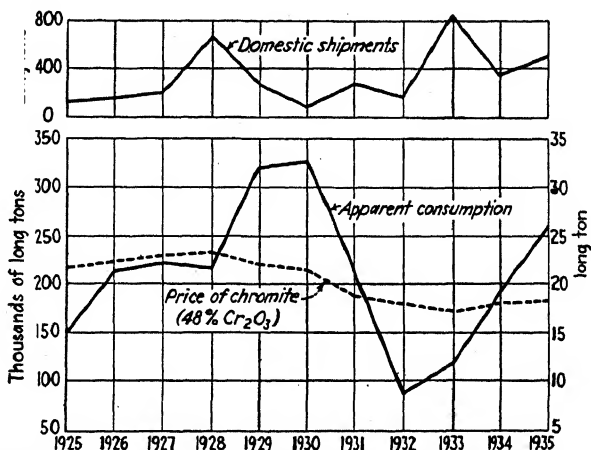


FIG. 1.—TRENDS IN CONSUMPTION, PRICE AND DOMESTIC SHIPMENTS OF CHROMITE IN THE UNITED STATES.

From Minerals Yearbook, 1936, U. S. Bureau of Mines.

### ANALYTICAL METHODS AND DATA

In Table 3 are given analytical data on chrome ores imported from various countries since 1929, together with the tonnages represented by the analyses. These tonnages do not represent the total imports for the year indicated.

The solution of chromite for analytical purposes is very difficult. For the determination of  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ , the best method of solution consists in fusion of a very finely ground sample with sodium peroxide in an iron crucible. For the determination of  $\text{FeO}$  a fusion with sodium peroxide in a silver or nickel crucible is required. Dr. G. Frederick Smith, of the University of Illinois, Urbana, Ill., has recently developed a new method for the solution of chrome ores, using a mixture of three parts of 85 per cent phosphoric acid and eight parts of 95 per cent sulphuric acid. This method is applicable when the sample weighs less than 150 mg. It is almost impossible, however, to completely dissolve larger samples, such as 0.5 gram, by means of this method, except by double treatment.

To determine  $\text{Cr}_2\text{O}_3$  the sodium peroxide fusion is boiled with water and acidified with sulphuric acid. The solution is completely reduced with standard ferrous ammonium sulphate and titrated with standard

potassium permanganate, using ortho-phenanthroline as an internal indicator.

To determine  $\text{SiO}_2$  the sodium peroxide fusion is boiled with water, acidified with perchloric acid, and evaporated to perchloric acid fumes. Water and hydrochloric acid are added and the solution boiled to remove impurities from the silica. The silica is filtered and the filtrate is evaporated to perchloric acid fumes a second time in order to remove all of the silica.

To determine  $\text{FeO}$  the sodium peroxide fusion, made in a silver crucible, is boiled with water and diluted to 500 c.c. in a volumetric flask. The solution is filtered and the residue is dissolved in dilute nitric acid. The silver is precipitated with hydrochloric acid, the solution is boiled to coagulate the silver chloride, and the latter is filtered off. The iron is determined in the filtrate.

To determine  $\text{Al}_2\text{O}_3$  the sodium peroxide fusion is boiled with water, diluted to 500 c.c. in a volumetric flask, the residue is allowed to settle, and the solution is filtered. C.P. ammonium chloride is then added to a 200 c.c. aliquot of the clear filtrate, and the solution is boiled. The resulting precipitate of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is removed by filtration and the required separation of the two is made.

The accurate determination of  $\text{CaO}$  and  $\text{MgO}$  in chromite is difficult. The sodium peroxide fusion is boiled with water to remove the hydrogen peroxide. The solution is then acidified with acetic acid just sufficiently to turn blue litmus paper red. The solution is boiled, diluted to 500 c.c. in a volumetric flask, and filtered, the  $\text{CaO}$  and  $\text{MgO}$  being determined in aliquots of the filtrate, the interfering elements remaining in the insoluble residue. This procedure is an adaptation of the basic acetate separation. The  $\text{CaO}$  and  $\text{MgO}$  are precipitated together as phosphates and then separated by the conventional methods.

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TABLE 3.—Analytical Data

Country	Year	Tonnage	Analyses, Per Cent*					
			Cr <sub>2</sub> O <sub>3</sub>	FeO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO
Brazil.....	1929	1,100	42.59 (±2.50)	15.82 (±1.50)	14.60 (±1.00)	7.38 (±1.00)	2.06 (±1.00)	15.39 (±1.00)
	1933	50	43.09 (±2.00)	16.77 (±1.50)	10.17 (±2.00)	8.32 (±1.00)	0.95 (±1.00)	17.98 (±1.50)
Canada.....	1934	44,000	31.34 (±1.50)	14.30 (±1.00)	26.86 (±3.00)	5.60 (±1.50)	0.31 (±0.75)	17.21 (±1.50)
	1935	35,000	31.45 (±0.60)	13.83 (±0.60)	26.57 (±1.00)	6.31 (±0.50)	1.20 (±0.50)	17.74 (±0.50)
	1936	50,000	30.48 (±2.50)	14.20 (±1.20)	27.48 (±2.50)	6.09 (±2.50)	0.38 (±0.60)	18.33 (±1.00)
	1929	24,000	37.43 (±0.10)	15.58 (±0.80)	21.40 (±2.25)	4.82 (±0.75)	0.75 (±0.30)	16.82 (±1.50)
Greece.....	1935	36,14	36.14 (±1.50)	15.43 (±0.60)	22.43 (±2.00)	5.24 (±1.30)	0.72 (±0.60)	15.96 (±1.75)
	1936	38,33	38.33 (±0.30)	15.70 (±0.35)	21.62 (±1.25)	4.68 (±0.20)	0.61 (±0.50)	16.48 (±0.10)
Lalapanzi (Africa).....	1930	400	46.63 (±1.15)	19.53 (±0.20)	13.64 (±0.70)	4.74 (±1.50)	0.43 (±0.30)	11.65 (±1.25)
Philippines.....	1935	200	54.39 (±1.00)	14.12 (±1.00)	11.62 (±1.00)	2.54 (±0.50)	0.55 (±0.30)	16.05 (±1.00)
	1936	1,000	32.09 (±1.90)	13.00 (±0.25)	27.61 (±1.50)	5.51 (±0.40)	1.05 (±0.30)	18.18 (±1.50)
Rhodesia (Africa).....	1934	35,000	45.43 (±0.45)	15.05 (±1.15)	13.84 (±4.00)	7.43 (±1.25)	0.46 (±0.35)	15.63 (±2.50)
	1935	51,000	44.93 (±2.50)	15.20 (±0.80)	12.94 (±0.60)	7.74 (±1.15)	0.53 (±0.60)	14.30 (±1.50)
	1936	70,000	46.43 (±2.50)	12.81 (±0.75)	15.42 (±2.50)	7.02 (±1.30)	0.38 (±0.80)	13.69 (±1.40)
	1930	13,000	39.08 (±1.00)	14.74 (±0.25)	15.63 (±2.50)	7.72 (±0.30)	1.15 (±0.50)	16.39 (±1.00)
Russia.....	1933	12,000	40.02 (±1.00)	14.11 (±0.10)	15.33 (±2.50)	10.06 (±0.30)	0.35 (±0.30)	16.47 (±0.75)
	1934	20,000	46.19 (±1.50)	15.63 (±0.75)	14.58 (±2.00)	3.96 (±0.30)	0.31 (±0.15)	15.39 (±1.50)
Serbia.....	1930	20,000	47.72 (±2.10)	12.22 (±1.75)	12.49 (±1.85)	6.18 (±2.60)	0.86 (±0.75)	15.89 (±2.90)
Transvaal (Africa).....	1930	7,000	44.89 (±1.50)	24.99 (±1.75)	14.71 (±1.50)	2.21 (±1.50)	0.76 (±0.50)	10.52 (±0.90)
	1934	17,000	45.02 (±1.50)	25.73 (±1.75)	15.05 (±1.50)	1.76 (±0.50)	0.74 (±0.40)	9.92 (±0.35)
Turkey.....	1930	3,600	46.95 (±2.50)	12.46 (±1.00)	13.45 (±1.00)	7.32 (±1.30)	1.99 (±0.75)	19.15 (±2.00)
	1932	23,000	40.51 (±0.40)	12.46 (±1.00)	10.95 (±0.75)	11.86 (±2.50)	0.86 (±0.30)	20.00 (±2.00)
	1933	32,000	46.57 (±2.50)	12.89 (±1.00)	12.50 (±1.00)	6.74 (±1.50)	1.16 (±0.50)	17.25 (±2.00)

\* Figures in parentheses indicate range of analyses.

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## CLAY

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THE term "clay" is usually applied to certain earthy rocks whose most prominent property is that of plasticity when wet. This permits them to be molded into almost any shape, which they retain when dry. Furthermore, they harden under fire. Clays contain certain hydrous aluminum silicates—the clay minerals—in appreciable amounts, but aside from this a number of other mineral grains, particularly quartz, may be present. Texturally clays are fine grained, and the so-called true clay particles are under  $2\ \mu$  in diameter.

## MINERALS IN CLAY

Certain hydrous aluminum silicates that predominate in many clays are known as the clay minerals<sup>66, 67</sup> and include: kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), dickite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), nacrite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), halloysite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), allophane ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), beidellite ( $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), nontronite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ), and montmorillonite [ $(\text{Mg}, \text{Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ].

Kaolinite, dickite and nacrite are known as the kaolin minerals, and although they have the same chemical composition, crystallize in the same system, show the same orientation of the axial plane A, and similar indices of refraction, they differ somewhat in their other optical properties. Individually they show characteristic X-ray diffraction patterns, dehydration curves, and behavior towards dyes.<sup>67</sup>

In studying the dehydration curves of kaolinite and anauxite, Ross and Kerr found that they show nearly flat curves up to a sharp break at  $390^\circ$  to  $450^\circ\ \text{C.}$ , following which there is a rapid loss of water up to about  $525^\circ\ \text{C.}$ , when the curves flatten out again with slight continued loss until complete dehydration at  $700^\circ$  to  $750^\circ\ \text{C.}$  Dickite showed an almost flat curve until just above  $500^\circ\ \text{C.}$ , when there is a strong loss up to  $575^\circ\ \text{C.}$ , at which point it flattens out again. Nacrite showed a slower loss of water than the other two, with the second break in the curve at  $675^\circ\ \text{C.}$ <sup>67</sup>

The term "anauxite" has been applied to some minerals having the same optical and crystallographic properties as kaolinite, but differing from it in having an alumina-silica ratio approaching 1:3. Apparently

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it forms an isomorphous series with kaolinite.<sup>67</sup> Pholerite, which has at times been used in the literature, sometimes to apply to kaolinite, is now discarded, as is also the name Newtonite. Leverrierite is the same as beidellite.

Kaolinite is commonly formed by the weathering of other minerals, particularly feldspar. Dickite seems to be the result of hydrothermal action, but may be formed at times by waters of meteoric origin, while nacrite so far as known always owes its origin to hydrothermal activity.<sup>67</sup> Halloysite is crystalline, as shown by the X-ray, and has a number of lines in common with kaolinite, but some are different. It always appears to be a weathering product, is very fine grained, white, and approximately isotropic, with an index near quartz. Its association with kaolinite is common.<sup>68</sup> Allophane is commonly glassy and amorphous, and not infrequently occurs as incrustations and thin seams alternating with halloysite, into which it may possibly change. Ross and Kerr consider it to be a solid solution of silica, alumina and water.<sup>68</sup> Montmorillonite, which is a common alteration product of the glassy particles of volcanic ash, appears in most places to have been formed by the action of sea water, since it is found in marine sediments, but in other instances may be the result of weathering.<sup>66</sup> Beidellite may also be derived from volcanic ash, but it is more abundant in ordinary clays and shales, in which it seems to have been derived from the weathering of mixed detrital material.<sup>66</sup>

Petrographers have also detected a "sericite-like mineral" in clay, for which the name illite has been recently suggested by Grim.<sup>24,66</sup>

It seems probable that the clay minerals may exert an influence on the physical properties of clay. Beidellite, for example, is thought to increase the bonding qualities.

Many other minerals have been identified in clays, but few of them occur in quantity.<sup>67</sup> Those that may be present, sometimes in appreciable amounts, are: quartz, usually in grains of variable size; calcite, usually in fine-grained, perhaps colloidal, form, but sometimes as concretions; limonite, often finely distributed as a coating on grains, sometimes as concretions or crusts; gypsum, in grains, selenite plates, crystals or rosettes; siderite, sometimes finely distributed, or occasionally as concretions in some clays and shales; pyrite as grains and concretionary lumps; muscovite, widely distributed, and commonly in very small flakes; rutile, almost universally present, but only in scattered grains of microscopic size.

While the clay minerals may form in place from the other minerals in residual or even some sedimentary clays, in some instances undoubtedly they originate under other conditions, as through the combination of colloidal alumina, silica and water. Thus Ross and Kerr describe long grains or worms of kaolinite noted in some Coastal Plain sands, which



could not have been transported and did not originate from the quartz grains.<sup>67</sup> There is also good evidence that kaolinite may replace quartz, as in the indianite deposits of Indiana,<sup>59</sup> and other places.<sup>67</sup>

The mineralogist commonly regards clays as made up of mineral grains, some of which may be very small, while the chemist and soil technologist frequently refer to them as consisting largely of colloidal particles, without any reference to a mineral composition. Thus Meyer<sup>44</sup> speaks of clay particles as being formed by the partial or complete combination of weak acids and weak bases, the proportion in which these are combined depending on the pH value of the surrounding medium. The clay particle, furthermore, he considers as consisting of a core made up of one or several molecules,\* carrying on its surface basic or acidic groups, or atoms, or positive or negative ionic charges, or both. Outside of this is the micellar ion atmosphere with adsorbed or unadsorbed ions. These together constitute the micelle. Basic and acidic atoms or groups are held on the surface of the clay particle by valence bond.

*Effect of Electrolytes.*—When thoroughly broken down or dispersed, the particles making up a clay cover a wide range of sizes. Some settle from a dilute suspension in a few minutes, but others, on account of their very small size, remain in suspension for a long time. These clay particles are negatively charged, and may be affected by small amounts of electrolytes, which exert an important influence on their settling properties. Some tend to increase the charge on the clay particles and help to keep them in suspension or dispersed. Such electrolytes are known as dispersing, deflocculating or peptizing agents. Other electrolytes have the opposite effect, in that they tend to reduce the charge on the clay particles, so that they unite, flocculate or coagulate. These may be called coagulating agents, and they reach their maximum effect when the negative charge on the clay particle is reduced to zero.

Clays do not all respond in the same manner to acids or alkalies, because each one may show its own acidity or alkalinity. Furthermore, the presence of soluble salts may exert a modifying effect. Dispersing electrolytes include sodium silicate, sodium hydroxide, sodium carbonate, sodium oxalate, sodium phosphate, etc. Coagulants include acids, sodium chloride, calcium chloride, aluminum chloride, etc. Some electrolytes, like sodium carbonate, may cause deflocculation when added to the clay in small amounts, and coagulation when larger amounts are added.

*Base Exchange.*—This process, representing the alteration in cation composition of a solid when treated with a salt solution, is probably of much importance in clays. According to the definition, base exchange may operate with either colloidal particles or larger grains of mineral

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\* Meyer states (personal communication) that these molecules may have the composition of clay minerals.

matter; in other words, it may operate in the weathering of rocks or in fine-grained sediments. Opinions seem to differ as to whether base exchange involves a change in crystal structure. It is probable, however, that it may go on in clays either during or after deposition, and Ross and Kerr<sup>67</sup> assert that it may take place without any breakdown of the clay molecule as a whole. The former suggests that certain clay minerals and zeolites possess so open a crystal lattice that certain cations can be displaced and other bases substituted in their place without disruption of the primary space lattice. Marshall<sup>41</sup> believes that this is the type of base exchange shown by most clays. He has measured the double

TABLE 1.—*Analyses of Clays*

	1	2	3	4	5	6	7	8	9	10	11	12
SiO <sub>2</sub> ...	46.3	45.78	57.62	59.92	68.62	82.45	54.64	38.07	47.92	49.56	53.12	90.00
Al <sub>2</sub> O <sub>3</sub> ...	39.8	36.46	24.00	27.56	14.98	10.92	14.62	9.46	14.40	15.08	18.72	4.60
Fe <sub>2</sub> O <sub>3</sub> ...		0.28	1.90	1.03	4.16	1.08	5.69	2.70	3.60	3.44	1.12	1.44
FeO....		1.08	1.20									
CaO....		0.50	0.70	tr.	1.48	0.22	5.16	15.84	12.30	1.08	1.40	0.10
MgO....		0.04	0.30	tr.	1.09	0.96	2.90	8.50	1.08	7.84	6.92	0.10
K <sub>2</sub> O....		0.25	0.50	0.64	3.36		5.89	2.76	1.20		5.72	tr.
Na <sub>2</sub> O...			0.20						1.50		tr.	tr.
TiO <sub>2</sub> ...						1.00			1.22	0.40		0.70
H <sub>2</sub> O....	13.9	13.4	10.5	9.7	3.55	2.40	3.74	2.49	4.85	22.96	12.04	3.04
Moist...		2.05	2.7	1.12	2.78		0.85					
CO <sub>2</sub> ....							4.80	20.46	9.50			
SO <sub>4</sub> ....			0.35						1.44 <sup>a</sup>			

<sup>a</sup> Also 1.34 organic matter.

- |                                       |  |
|---------------------------------------|--|
| 1. Kaolinite.                         | 8. Brick clay, Milwaukee, Wis.                 |
| 2. Washed kaolin, Webster, N. C.      | 9. Shale clay, Ferris, Tex.                    |
| 3. Plastic fire clay, St. Louis, Mo.  | 10. Bentonite, Otay, Calif.                    |
| 4. Flint fire clay, Salineville, Ohio | 11. Potash-bearing bentonite, High Bridge, Ky. |
| 5. Loess, Guthrie Center, Ia.         | 12. Sandy brick clay, Colmesneil, Tex.         |
| 6. Siliceous clay, Rusk, Tex.         |  |
| 7. Brick shale, Mason City, Ia.       |  |

refraction of clay particles as small as 50  $m\mu$  ( $m\mu = 0.00001$  mm.) and finds that it varies according to the cation present. Such measurement is possible in clays whose particles show oriented coagulation, and works accurately for particles smaller than 500  $m\mu$ . He also notes that clays with high base-exchange capacity have a greater capacity for oriented coagulation.

Sodium chloride solution in contact with an ordinary clay results in a displacement of some of the calcium or magnesium in it. Conversely calcium or magnesium may displace sodium. Only clay minerals with easily replaceable bases, such as calcium, magnesium, potassium or sodium, exhibit much base exchange. Montmorillonite is quite susceptible to it.

*Chemical Composition.*—Clays vary widely in their chemical composition, from those close to kaolinite to others that show a high percentage of impurities. Table 1 shows this variation. A chemical analysis of clay is not usually carried out in detail, so that the  $\text{TiO}_2$  is included with the  $\text{Al}_2\text{O}_3$ , instead of being determined separately. All volatile matter is commonly expressed as loss on "ignition." All iron is usually determined as  $\text{Fe}_2\text{O}_3$ . Other unsatisfactory features of the chemical analysis are that it gives us little information regarding the physical properties of the clay, or the distribution of the constituents in the samples analyzed.<sup>57</sup> Moreover, it is unsafe to attempt to calculate the mineral composition from the bulk analysis. A modification of the ordinary quantitative analysis, known as the "rational analysis," attempts to determine the compounds present. It was first applied to kaolins, which were assumed to consist of quartz, feldspar and kaolinite (clay substance). The method is not reliable, however, and no satisfactory way of making this type of analysis has been devised.<sup>57</sup>

#### PROPERTIES OF CLAY

*Plasticity.*—The property of plasticity, already defined, is the outstanding characteristic of clays. They vary from those of high plasticity, or "fat" ones, like the ball clays and bonding clays, to those of low plasticity, termed "lean," and represented by some very sandy ones. The plasticity may be affected by the amount and character of colloidal material, the quantity and proportions of nonplastic particles, the amount of water, as well as salts, bases, acids and organic matter.

The cause of plasticity has been much discussed<sup>46,57</sup> and has been variously assigned to hydrous aluminum silicates, shape and size of grains, colloidal content, etc. The present general view regarding plasticity is well expressed by Norton, who says: "It is undoubtedly due to an active particle surface, which has the property of attracting to it a stable water film. This attractive force both holds the water in the pores and the particles together." There is no doubt also that the plasticity is influenced by the thickness and viscosity of the water films around the particles, as well as the size, shape and distribution of the latter.

The plasticity of a clay may be reduced by the addition of nonplastic material. Preheating a clay before use, to temperatures varying from  $100^\circ$  to  $300^\circ$  C., has a similar tendency.<sup>9</sup> Greaves-Walker found that the addition of hydrochloric acid to North Carolina shales increased their plasticity.<sup>23</sup>

While the particle size has sometimes been suggested as the chief cause of plasticity, it has been pointed out by Parmelee that mixtures of very fine-grained clays and coarse-grained ones are more plastic than either of these alone.<sup>46</sup> Very fine grinding of some minerals gives some plasticity, but nothing like that observed in clays. It is also claimed that an excessively high colloidal content develops stickiness but not plasticity.

*Texture.*—The grains of clay cover a relatively wide range of size, some clays containing sand particles large enough to be recognizable with the naked eye. A large percentage of the particles may be less than  $2\mu$  (0.002 mm.) in size, and when the clay is thoroughly dispersed the smallest, which are negatively charged, may remain in suspension for days.

In most ceramic work the separation of the particles in a clay is commonly made with sieves, some as small as 300 mesh. The Bureau of Public Roads uses the hydrometer test to determine the sizes from sand down, and Table 2 gives such a series. By using a super-centrifuge,

TABLE 2.—*Mechanical Analyses of Clays Made by Hydrometer<sup>a</sup>*

No. <sup>b</sup>	Particles Larger than 2.0 Mm.	Coarse Sand, 2.0 to 0.25 Mm.	Fine Sand, 0.25 to 0.05 Mm.	Silt, 0.05 to 0.005 Mm.	Clay Smaller than 0.005 Mm.	Colloids Smaller than 0.001 Mm.	Passing No. 40 Sieve
1	10	51	25	16	8	6	65
2	3	26	45	16	13	9	85
3	1	14	34	28	24	1	90
4	3	6	23	57	14	0	96
5	0	3	3	6	88	78	97
6	0	1	14	52	33	16	100
7	0	2	9	43	46	22	100
8	0	0	1	14	85	80	100

<sup>a</sup> Supplied by U. S. Bureau of Public Roads.

<sup>b</sup> 1. Sandy clay from South Carolina. 2. Sandy clay from Madison County, Virginia.  
3. Frost-heaving silt soil from New Hampshire. 4. Frost-heaving silt soil from Oregon.  
5. Colloidal clay soil productive of landslides in Virginia. 6. Expansive clay from Kansas.  
7. Gumbo from Red River Valley, Minnesota. 8. Wyoming bentonite.

Marshall<sup>41</sup> has separated the smallest particles of clays, as shown in Table 3. These clays, after removal of organic matter, soluble salts and exchangeable bases, were dispersed after bringing to pH 9 with NaOH.

TABLE 3.—*Mechanical Analyses of Clays by Centrifuge Method*

Clay	Concentration, Per Cent	2 $\mu$ –1 $\mu$	1 $\mu$ –0.5 $\mu$	500–200 $\mu\mu$	200–100 $\mu\mu$	100–50 $\mu\mu$	Under 50 $\mu\mu$
Kaolin.....	0.2	66.0	21.0	7.0	6.0	39.0	
Bentonite <sup>a</sup> .....	1.0	2.0	31.0	16.0	12.0		
Putnam clay.....	0.5	7.8	6.6	11.8	11.6	21.3	40.9
Rothamsted.....	0.5	15.2	12.1	18.7	14.3	10.3	29.4

<sup>a</sup> Approximate values obtained by interpolation in the distribution curve.

*Water in Clay.*—Two kinds of water are usually recognized in clay: (1) mechanically held water, and (2) chemically combined water.

When a clay dries from its plastic condition to a constant weight at room temperature, the water that evaporates until air shrinkage ceases is known as "shrinkage water." That which is still left in the intergrain spaces is termed "pore water," and may be driven off at 110° C. The pore water and shrinkage water together are known as the "water of plasticity." There may also be moisture retained on the surface of the clay particles as a film of molecular dimensions, which is tenaciously held and which is referred to as hygroscopic or micellar water. It may not all pass off until the clay is heated to 200° C. Table 4 gives the range of water of plasticity as recorded for a number of types of clay.<sup>57</sup>

TABLE 4.—*Water of Plasticity of Clays*

	PER CENT		PER CENT
Crude kaolin.....	36.39-44.78	Plastic fire clay.....	13.00-37.00
Washed kaolin.....	44.48-47.50	Flint clay.....	9.00-19.00
White sedimentary kaolin....	28.60-56.25	Brick clay.....	13.00-41.00
Ball clay.....	25.00-53.00	Sewer-pipe clay.....	11.00-36.00
Crucible clay.....	27.00-51.00		

A high percentage of shrinkage water is rather characteristic of fine-grained clays that dry to a strong body, and they are also likely to show excessive plasticity, high shrinkage, warping and cracking. A high content of pore water characterizes a clay with a porous structure. The ratio of shrinkage water to pore water is said to be important in clays used in the manufacture of crucibles and glass pots,<sup>46</sup> and the best ones are said to show a ratio of 1:1 between shrinkage water and pore water. Table 5 gives the properties of several clays with respect to water and shrinkage.<sup>46</sup>

TABLE 5.—*Water and Shrinkage in Clays*

Clay	Water Plasticity	Volume Drying Shrinkage	Shrinkage Water	Pore Water	Ratio Pore Water to Shrinkage Water
Kentucky ball....	54.8	30.3	28.8	26.0	0.90
S. P. G. ball.....	48.2	25.0	21.5	26.7	1.24
English ball.....	40.9	25.8	21.1	19.7	0.93
Georgia kaolin....	33.5	15.3	11.4	22.0	1.93
Missouri Hercules	30.3	18.3	12.7	17.6	1.38

Clay is very hygroscopic and when dry absorbs moisture from the atmosphere, some absorbing as much as 10 per cent of its dry weight. The chemically combined water is chiefly that held in combined form as a part of the hydrous aluminum silicates, and passes off mostly at a temperature of 450° to 600° C.

*Shrinkage.*—Clays exhibit two kinds of shrinkage, air and fire. Air shrinkage occurs as the clay dries and continues until the particles are all in contact. It depends in part on the water content, and character

of the clay, being high in very plastic clays and low in sandy ones. An excessive air shrinkage tends to cause cracking, but a low air shrinkage is usually characteristic of clays that dry to a weak and porous body.

Open porous clays are easier to dry than dense, highly plastic ones, for in the latter water evaporates from the surface more rapidly than it can be drawn from the interior, and this develops stresses, which cause cracking. Very plastic clays therefore require slow drying.

Air shrinkage may be recorded in terms of the length or volume of the dry clay, the two being called respectively linear and volume shrinkage. Both linear and volume shrinkage may be measured (see Tests), but the former can also be calculated from the latter.<sup>57</sup>

TABLE 6.—*Air Shrinkage of Clays*

Clay	Linear, Per Cent	Volume, Per Cent
Crude kaolin.....	5.00- 7.6	14.11-20.92
Washed kaolin.....	3.00-11.0	20.00-29.00
Georgia kaolin.....	4.50-12.5	7.50-36.46
Ball clays.....	5.25-12.0	22.00-32.00
Flint clays.....	0.78- 6.5	2.3 -21.00
Sagger clays.....	3.00-11.0	9.0 -25.00
Paving-brick clays.....	0.90- 6.0	3.5 -18.00
Sewer-pipe clays.....	3.50-10.5	16.12-22.90

*Strength.*—The strength of clay in its dried condition is an important property, as it enables it to withstand shocks in handling of the dried ware; also, a clay of high strength is capable of carrying a larger amount of nonplastic material, without too great deterioration of strength.

Strength of a dried clay may be determined by tension, compression, or transverse tests. The first was formerly much used, but is now discarded, the second finds little favor, while the third is the one commonly employed. It is expressed in terms of the modulus of rupture, and is carried out on the clay dried at 110° C., ranging in different clays from a few pounds per square inch to, in extreme cases, over 1000 lb. The figures in Table 7 give some idea of the range of transverse strength in different types of clays.<sup>57</sup>

TABLE 7.—*Range of Transverse Strength in Clays*

Clay	Lb. per Sq. In.
Washed kaolin.....	75- 200
Georgia sedimentary kaolin.....	150- 166
Ball clays.....	25- 600
Glass-pot clays.....	173-1068
Sewer-pipe clays.....	190- 589
Sagger clays.....	46- 474
Brick clays.....	50-1500

The transverse strength of most clays usually decreases when sand or ground flint is added but occasionally an increase in strength may result, because the clay alone develops minute cracks in drying, which weaken it. The addition of flint avoids this and the true strength of the clay manifests itself.<sup>46,57</sup> It has also been shown that the transverse strength of a clay may increase with an increase in its base exchange capacity.<sup>31</sup>

The bonding strength of a clay refers to its power to hold together particles of nonplastic materials, such as standard sand, potter's flint, or "grog" (crushed brick). The property is important in the use of pottery, glass-pot, and crucible clays,<sup>10</sup> as they have an appreciable amount of nonplastic material mixed with them.

*Color.*—Iron is the commonest coloring agent of raw clays, giving yellow, pink, reds and browns, depending on the amount present and the state of oxidation. Greensand usually gives a green color. Organic matter may color a clay gray or black—sometimes even pink. Clays free from these coloring agents are usually white. Fired clays may owe their color to iron compounds, titanium oxide, or lime reacting with iron, but iron is the usual cause of the color.<sup>46,57</sup>

The best white-burning clays have under one per cent  $\text{Fe}_2\text{O}_3$ , but some have 2 per cent, although the latter tend to develop a light cream tint. An exact prediction regarding the color-burning qualities cannot be made from the chemical analysis, partly because it does not show whether the iron is evenly distributed. Buff-burning clays may vary from 1 to 5 per cent  $\text{Fe}_2\text{O}_3$ , but just why this color may be obtained from such a wide iron range is difficult to explain. Most of them have 3 to 4 per cent  $\text{Fe}_2\text{O}_3$ . Red-burning clays have 5 per cent or more  $\text{Fe}_2\text{O}_3$ . Such clays at a low temperature tend to burn pale red or salmon, but as the temperature increases they turn to a darker red and finally purplish or even greenish purple. The more siliceous clays usually develop a brighter shade of red. Much depends on the kiln atmosphere, for if this is reducing iron gives a bluish or bluish black color. Some white, cream or buff-burning clays become bluish gray at certain temperatures, owing possibly to the formation of ferrous silicate. This is called bluestoning. Lime in excess of iron oxide, if the two are evenly distributed, gives a cream-colored product, unless overfired, when the clay turns greenish or greenish yellow. Before the iron and lime begin to react, the clay may be pink, if enough iron is present. Titanium oxide to the extent of perhaps 2 per cent causes a creamy tint. This may explain why some clays very low in iron oxide do not burn white.

*Porosity.*—The porosity of a clay refers to its volume of pore space expressed in terms of its total volume. In raw clay the pores are all open but of variable size. In fired clays the pores may be of variable size, but are of two types, open and closed, the latter being formed by the expansion of gases during fusion. Porosity in the raw clay influences

its drying qualities, in that large pores permit the water to escape more rapidly. In fired clays the shape and size of the pores affect the properties of the ware, such as strength, behavior as an absorbent, resistance to weathering, shock, abrasion, corrosion, discoloring agents, efflorescence, destructive action by fungus growths, dielectric strength, etc.<sup>46</sup>

The temperature-porosity relations in firing serve to show the manner and progress of vitrification. Thus a clay in which porosity decreases rapidly, because of sudden fluxing action, is one that vitrifies quickly, and when a rise of the porosity curve quickly follows the drop in porosity it indicates a short firing range, such as would be characteristic of highly calcareous clays.

It is not uncommon to determine the absorption of a fired clay for water, instead of its porosity, since the curve of the former in a general way follows the latter, but is always lower.

*Specific Gravity.*—The specific gravity of a clay may be expressed in three different ways:<sup>46,57</sup>

- 1. True specific gravity, or the ratio of solid material, exclusive of closed or open pores, to an equal volume of water. This is determined on a powdered sample.
- 2. Apparent specific gravity, or the ratio of the volume of solids (plus the volume of any closed pores) to an equal volume of water.
- 3. Bulk specific gravity, or the ratio of the entire volume of material, including solids, closed and open pores, to an equal volume of water.

True specific gravity is affected by the minerals present in the raw clay, and in the fired clay by silica inversion, chemical reactions, fusion and crystallization. The apparent and bulk specific gravity are affected by all of the above, as well as by the porosity. In firing, the true and apparent specific gravity should theoretically decrease, while the bulk specific gravity increases. Change in specific gravity during firing indicates progress of vitrification. Table 8 gives the change in porosity and specific gravity of a Maryland clay.<sup>58</sup> Table 9 gives another series of somewhat complete determinations made on Kentucky ball clay.

TABLE 8.—Changes in Specific Gravity and Porosity during Firing

Temperature, deg. C. ....	1150	1200	1250	1275	1300	1325	1350	1375	1400
Porosity, per cent. ....	22.8	22.0	10.1	9.6	6.6	6.3	1.4	0.7	0.4
Volumetric shrinkage, per cent. ...	8.0	8.9	19.1	20.8	17.6	16.1	19.3	19.5	19.5
Apparent specific gravity ....	2.52	2.51	2.42	2.44	2.32	2.29	2.24	2.25	2.25
Bulk specific gravity ....	1.94	1.96	2.18	2.21	2.17	2.14	2.22	2.23	2.24

If the sample tested is a manufactured product, the amount of water and pressure used in molding may influence the results. Therefore there will be a difference in the bulk gravity, depending on whether the ware is slip-cast, hand-molded, plastic, or dry-pressed, if the same material is used.<sup>46</sup>



*Firing Changes.*—When a clay is fired it undergoes various changes in color, hardness, specific gravity, porosity, etc. Some of these have already been referred to; others are mentioned below. These changes may begin at a relatively low temperature range, or they may not be completed until higher temperatures are reached.

TABLE 9.—*Determinations on Kentucky Ball Clay*<sup>a</sup>

Cone	2	6	8	10	12	14
Volume fire shrinkage, per cent....	31.6	34.9	36.7	38.7	39.4	42.2
Apparent porosity, per cent.....	21.8	15.8	9.5	2.9	1.1	1.2
Total percentage of pores based on bulk volume of piece.....	22.4	18.4		8.9	6.1	4.1
Closed pores.....	1.8	3.9		6.2	4.0	3.8
Specific gravity:						
Bulk.....	2.09	2.18		2.32	2.39	2.47
True.....	2.69	2.679		2.541	2.515	2.587
Apparent.....	2.65	2.57		2.38	2.41	2.49

<sup>a</sup> Made by Parmelee and McVay.

*Loss of Volatile Products.*—The volatile products liberated during the firing of clay consist of: (1) chemically combined water; (2) organic matter, either carbon or bituminous matter; (3) oxides of sulphur or carbon given off when carbonates, sulphates or sulphides are dissociated. Dehydration of hydrous aluminum silicates takes place chiefly between 450° and 600° C., there being a slight variation in the different ones.<sup>15,46,57</sup> Gibbsite shows from 25 to 30 per cent loss at 310° C., and diaspore, 12 to 14 per cent loss at 540° C. Hydrous iron oxides generally decompose at 150° to 250° C., although some show the change between 250° and 300° C. Hydrocarbons, which may give trouble in firing, may be completely oxidized and removed by heating at between 800° and 900° C. Calcium carbonate at normal atmospheric pressure decomposes a little below 900° C., although the change may begin earlier. Siderite decomposes at 800° C., but in presence of clay this may begin at 425° C.<sup>46</sup> Pyrite begins to decompose at 350° C., while gypsum loses three-fourths of its H<sub>2</sub>O between 250° and 400° F., and all of its volatile matter by 1100° C.

The two following analyses, representing (1) an impure clay from Ferris, Tex., and (2) brick from that clay, are interesting as showing the loss of volatile products in firing:<sup>53</sup>

	2		1	2
SiO <sub>2</sub> .....	49.45	56.8	Na <sub>2</sub> O.....	0.21
Al <sub>2</sub> O <sub>3</sub> .....	17.11	20.4	TiO <sub>2</sub> .....	0.17
Fe <sub>2</sub> O <sub>3</sub> .....	3.45	6.2	H <sub>2</sub> O.....	4.84
CaO.....	12.67	11.7	CO <sub>2</sub> .....	7.10
MgO.....	1.77	1.4	SO <sub>3</sub> .....	2.00
K <sub>2</sub> O.....	0.13	1.5		
			99.43	99.7

*Fusibility.*—When exposed to a rising temperature clays do not fuse suddenly; on the contrary, they soften slowly until the entire clay becomes a viscous mass. With impure clays this may occur at a relatively low temperature, but with those approaching kaolinite in composition, it takes place at a much higher one.

Following dehydration, the clay is porous, but after a temperature interval, it begins to compact, then the more easily fusible minerals begin to melt with the formation of glass. With further temperature rise the fluid portion attacks the mineral grains not yet fused, and finally we get a solution of molten glass.

In the first stages of firing, although the clay may become compacted into a hard mass like common brick, it is said by some that there is no evidence of softening of the particles.<sup>46</sup> This period has also been called incipient vitrification, but by some that term is used to refer to the stage at which enough glass has been developed to bind the mass together. Complete vitrification would represent the stage reached in the fusion of a clay when sufficient glass has been developed to close all the pores. As the temperature rises and the fluidity of the glass developed increases, the clay mass or object no longer holds its shape, and reaches a condition referred to as viscosity. The temperature at which the development of glass begins, as well as its amount and viscosity, exerts an influence on the behavior of the clay during vitrification. In some clays glass has been found to develop at a temperature as low as 700° C. The term vitrification as applied to clay wares does not always mean the same thing. Paving brick and sewer pipe, for example, are said to be vitrified, but technical difficulties prevent the complete attainment of this condition. Electrical porcelain must approach it very closely.

The stages of incipient vitrification, vitrification and viscosity merge into each other, but the temperature interval between the first point and overfiring is variable. Clays having a long vitrification range are, in general, the safest to use for vitrified wares, as most commercial kilns cannot be controlled within a range of a few degrees of temperature, and there is less danger of the ware becoming overfired and ruined. Clays that begin to overfire as soon as they have reached a condition of vitrification are said to have a short firing range.

The curves of porosity and fire shrinkage shown in Figs. 1 and 2 illustrate well the behavior in firing of the two types of clay mentioned above.

Most fired-clay bodies when examined in thin section under the petrographic microscope show a variable amount of glass, depending on the amount of fusion that has taken place during firing, while scattered through this there will be noticed mineral grains that have not yet been affected. Some of these, however, may exhibit a certain amount of corrosion.

Relatively few new minerals will have been found to have crystallized out from the fused material on cooling. Small rods of hematite have been observed in the glassy matrix of some ferruginous clays, but the mineral that has been most often noticed, and which has attracted considerable attention, consists of needlelike grains, usually colorless. For some years these were identified as sillimanite, but later it was discovered that they were the mineral mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). The temperature at which this develops does not seem to be the same always, but it has been observed to form at as low as  $900^\circ\text{C}$ . Mullite is a rare mineral, having been first observed in some igneous rocks on the island of Mull. Commercial

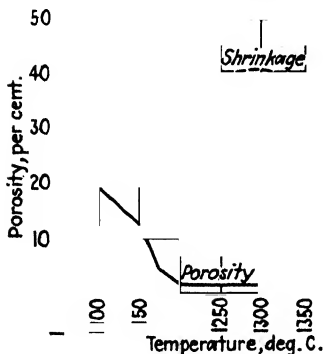


FIG. 1.

FIG. 1.—POROSITY AND SHRINKAGE CURVES OF A TENNESSEE BALL CLAY WITH LONG FIRING RANGE.

Bleining and Loomis: *Trans. Amer. Ceramic Soc.* (1917) 19.

FIG. 2.—POROSITY AND SHRINKAGE CURVES OF CLAY WITH SHORT FIRING RANGE.

Brown: *Jnl. Amer. Ceramic Soc.* (1918) 1.

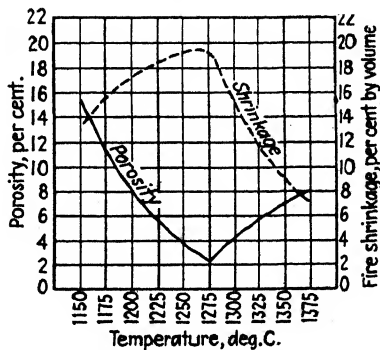


FIG. 2.

deposits are found of the minerals sillimanite, kyanite and andalusite, all of which have the composition  $\text{Al}_2\text{SiO}_5$ . When these are heated they all change to mullite at temperatures between  $1400^\circ$  and  $1550^\circ\text{C}$ . It has been found that the development of mullite in the firing of certain ceramic bodies has great importance, because it imparts to the ware high tensile strength, superior dielectric properties, and low thermal expansion, properties that are particularly valuable in spark plugs. It is possible to use the proper amount of the minerals mentioned in the clay mixture and have them change to mullite in firing.

The fusion point of a clay is usually expressed in terms of Seger cones,<sup>67</sup> and may range from as low as perhaps cone 1 ( $1150^\circ\text{C}$ .) to cone 35 ( $1785^\circ\text{C}$ .).

**Soluble Salts.**—Many clays contain at least a small percentage of water-soluble inorganic compounds, which are brought to the surface in the drying of the ware, remaining there as a coating, usually white. These soluble salts are mostly sulphates of lime and magnesia, but sometimes others. Vanadium salts may also cause a stain.<sup>71</sup> Soluble salts may be in the clay when taken from the ground, or they may form as the

result of weathering, as when pyrite is present. They may also be introduced in the water used for mixing the clay. Others may be formed during firing, by the kiln gases carrying oxides of sulphur from the fuel, which, coming in contact with carbonates in the clay in the presence of moisture, convert them into sulphates.<sup>46, 58</sup>

Soluble salts in clays range from zero to 1.5 or 2.0 per cent.<sup>46</sup> They may be the cause of technical troubles because of: (1) the unsightly coating that they form on some wares, (2) interference with the adherence of a glaze, and (3) the crystallization of these salts in the pores of the product may cause its disintegration. Barium compounds are sometimes added to the clay to render the obnoxious salts insoluble.

### ORIGIN OF CLAY

Clays may originate from different kinds of rocks, either by the ordinary processes of surface weathering or by the action of solutions, which may be of igneous origin or indirectly of surface origin. In both cases the alteration product is of residual character, and the material may be called a residual clay.

The removal of the clays so formed by various agents of erosion and transportation and deposition elsewhere gives rise to a great group of transported clays.

The several ways in which clay deposits originate are brought out by the accompanying classification.<sup>57</sup>

### *Classification of Clays*

#### A. Residual clays.

Formed by weathering of rocks *in situ*, or by rising solutions of magmatic or meteoric origin.

##### I. Kaolins, white and firing white or light cream.

- a. Deposits roughly tabular in form, as when derived from pegmatites, or hydrothermal alteration along fractures.
- b. Blanket deposits from areas of igneous or metamorphic rocks.
- c. Replacement deposits, as Indianaité.
- d. Bedded deposits from feldspathic sandstones.

##### II. Red-burning residuals, derived from different kinds of rocks.

#### B. Colluvial clays, practically landslide masses.

#### C. Transported clays.

##### I. Deposited in water.

- a. Marine clays or shales. Deposits often of great extent.

White-burning clays; ball clays and sedimentary kaolins; refractory clays or shales; buff burning

Impure clays and shales  $\left\{ \begin{array}{l} \text{Calcareous.} \\ \text{Noncalcareous.} \end{array} \right.$

- b. Lacustrine clays deposited in lakes or swamps.

Fire clays or shales.

Impure clays or shales, red burning.

Calcareous clays, usually surface deposits.

- c. Flood-plain clays. Recent ones usually impure and somewhat sandy.

d. Estuarine clays (deposited in estuaries), mostly impure and finely laminated.

e. Delta deposits. Variable purity, often lenticular.

II. Glacial clays found in the drift. Often stony and lacking stratification. May be red or cream burning (calcareous).

III. Wind-formed deposits (some loess).

D. Chemical deposits (doubtful origin).

*Residual Clays.*—Those due to weathering may be formed: (1) by the decomposition of the silicate minerals in rock, the product being a clay; (2) by the solution of a carbonate rock containing clayey impurities, which are left behind as an insoluble residue, and (3) by the disintegration, accompanied occasionally by some solution, of shales.

In case 1, where the decomposition of silicates like feldspar is involved, the clay mineral formed is a hydrous aluminum silicate, such as kaolinite. Residual clays formed by weathering overlie the bedrock formation from which they have been derived. They may grade into it, as is usual when the weathering of silicate rocks is involved, or there may be an abrupt change from clay to bedrock, as in those derived from limestones. While residual clays have formed throughout geologic time, relatively few "fossil" deposits are found, since these clays are easily removed by erosion.

The thickness of such clays is variable and depends on the depth to which weathering has penetrated the rock, and the freedom of the deposit from erosion. Residual clays derived from rocks free or nearly free from iron-bearing minerals are white and represent the true kaolins but most residual clays are stained by oxides of iron.

Laterite is a peculiar type of residual clay, formed under such conditions that silica is largely removed during weathering, leaving alumina and iron hydroxides predominating in the residual mass. Its formation is associated with tropical climates, and a variety of rocks may yield it.<sup>83</sup>

Residual clays, usually of ferruginous nature, are found in many parts of the United States, particularly east of the Mississippi and south of the glaciated area. Within the latter they occur only in protected situations.

Kaolins are confined mainly to the belt of crystalline rocks of the Atlantic States from Delaware southward, and reach their greatest importance in western North Carolina. Commercially important deposits are also known at one locality in Quebec, and near Spokane, Wash. In England, the largest deposits known are in the Cornwall district, and these have for years been a large contributor to the American pottery industry. Residual clays formed by rising waters are relatively rare, and not as a rule of commercial value. However, such an origin has been ascribed by some to the Cornwall deposits, and those of Karlsbad, Czechoslovakia, as well as the Quebec and Washington occurrences.<sup>28,96</sup>

*Transported Clays.*—Transported clays initially were derived from residual clays, but later on in addition from pre-existing sedimentary

deposits. As noted in the classification, they have been deposited chiefly in water, under a variety of conditions, which affect the extent and also the characters of the deposit. Those of recent geologic age are usually unconsolidated, but the older ones from the Tertiary downwards are often consolidated to shales, although there may be noticeable exceptions, as in some Tertiary and Cretaceous deposits of the United States.

Glacial clays are of limited occurrence and confined to the area of Pleistocene glaciation.

Wind-formed deposits, if this origin is accepted for the loess, are of widespread occurrence in the Great Plains area. Chemical deposits are a debatable group, in so far as workable ones are concerned.

*Secondary Changes in Clay Deposits.*—In areas of crustal disturbance, beds of sedimentary clays and shales are sometimes folded and faulted, and this may result in steeply dipping beds, as along the eastern edge of the Rocky Mountains. Some Paleozoic shale formations of the eastern United States show a regional dip. Weathering may often bring about such changes as leaching of lime carbonate, oxidation of the iron compounds, or opening of the structure. The transportation and redistribution of iron oxide by surface waters may cause the formation of crusts, and sometimes concretionary masses. Chert concretions are found in residual clays, but most concretions found in sedimentary clays are probably of contemporaneous origin, and may consist of limonite, iron carbonate or lime carbonate.

Shale beds in places are so softened by weathering near the outcrop that they easily yield a plastic mass when ground and mixed with water, but with depth the material may become much harder and occasionally have too little plasticity to be workable.

#### DISTRIBUTION OF CLAYS AND SHALES

Clays and shales are widely distributed in the United States and Canada, in formations ranging from pre-Cambrian to Recent. The more important types are:

*Kaolins.*—In their washed condition, kaolins are used in the manufacture of high-grade products, such as white earthenware, porcelain of all kinds, as well as fillers. They are rather limited in their distribution.

Kaolins resulting from the weathering of pegmatite are found in the belt of crystalline rocks extending from Delaware to Georgia,<sup>59</sup> but the only important deposits now worked are those of western North Carolina, and to a lesser extent Delaware. The pegmatites of North Carolina may be weathered to a depth of 80 to 100 ft. White residual clays derived from the Oriskany limestone have been worked near Saylorsburg, Pa., and others formed from schist were mined at South Mountain, Pa.<sup>60</sup> Kaolins from weathered dolomite have been mined in southeastern Missouri.<sup>60</sup> A group of deposits near Spokane, Wash., formed from pegmatite have been used for refractory wares.<sup>66</sup>

In Canada, the only kaolin deposit worked is near San Remi, Que. This is unique in that it is supposed by some to have been formed by the replacement of quartzite, caused by hydrothermal activity.<sup>29</sup>

The so-called sedimentary kaolins occurring in the Cretaceous of Georgia<sup>74</sup> and South Carolina,<sup>90</sup> have been worked for a number of years, being used in the manufacture of white pottery, refractories and as a filler. The deposits are usually lens-shaped and may be of considerable extent, as well as thickness. Bauxite is associated with some. The product may be washed before shipment to market.

A widely used clay, intermediate in its properties between true kaolins and ball clays, is an extensive deposit of white sedimentary clay occurring in the Tertiary (Eocene) of north central Florida.<sup>6</sup> It has been worked for over 40 years, and is known to underlie several counties. The material is exceedingly sandy, and is washed before shipment.<sup>6,59</sup>

*Ball Clays.*—These are sedimentary, plastic, refractory clays, which fire white or nearly so, and are used chiefly as one of the ingredients of whiteware, as well as for other purposes where a refractory clay of good bonding power is required.<sup>77</sup> The chief domestic supply comes from the Tertiary formations of western Kentucky and western Tennessee,<sup>45,59</sup> where the material occurs as large lenses associated with other refractory clays used for such purposes as firebrick, saggers, bond for abrasives, etc. These different grades may form separate layers at times in the same deposit.<sup>59</sup> A relatively small amount of ball clay is also obtained from the Cretaceous beds of New Jersey.<sup>61</sup>

The only locality in Canada where ball clay is said to occur is in southern Saskatchewan, and this is remote from important markets.<sup>42</sup>

*Fire Clays.*—Under this head are included all refractory clays, exclusive of kaolins and ball clays. Sedimentary clays of this character are found in the United States in formations ranging from the Carboniferous to Tertiary, exclusive of the Triassic.<sup>18</sup> Their geologic distribution in Canada is restricted to the Cretaceous and Tertiary.

Foremost among the clays of this group are those found in the Carboniferous of Pennsylvania,<sup>72</sup> Ohio,<sup>5,1</sup> Kentucky,<sup>54</sup> Missouri,<sup>85,91</sup> Indiana,<sup>92</sup> Illinois,<sup>32,47</sup> and Maryland.<sup>50,88</sup> The clays occur at a number of different horizons, and may be associated with coal. Most of the material is plastic fire clay, but with it there may be a hard type known as flint clay, which develops little plasticity, and which, because of its texture, structure and appearance, has received this special name. It is found particularly in Pennsylvania, Ohio, Maryland and Kentucky. Many of these fire-clay deposits are worked as open pits, but others are reached by drift or shaft. These clays are widely used for firebrick.

The Lower Cretaceous formations of New Jersey have for years supplied material for the refractory-products industry.<sup>60</sup> They are all plastic clays and are unassociated with coal. In Texas<sup>53</sup> and Mississippi,<sup>59,39</sup> the

Tertiary formations supply refractory clays. Those from the latter state have found favor because of their high bonding qualities, of value in the manufacture of glass pots and crucibles. Other Tertiary clays have been developed in California,<sup>19,78</sup> Washington,<sup>94</sup> and Colorado.<sup>17</sup> A unique type of refractory clay is that found in the north central Ozark region of Missouri,<sup>4</sup> where there is a series of basin-shaped deposits carrying flint clay, and some run rather high in diaspore. These diaspore clays, which Allen thinks have been formed by the alteration of the flint clay by the action of percolating solutions containing CO<sub>2</sub>, are of highly refractory character. Clays intermediate in alumina content between flint clay and diaspore are called burley clays in the Missouri district. The No. 1 grade is said to carry 60 to 70 per cent alumina.<sup>66</sup>

In Canada fire clays have not been as widely developed, nor are they as widely distributed, as in the United States. The most important deposits are those south of Moosejaw and in southern Saskatchewan. Extensive deposits are also known to occur and have been worked around Clayburn, in southwestern British Columbia. A curious series of deposits is known to have been preserved under a heavy cover of glacial drift on the Mattagami and Missinabi Rivers<sup>20,30</sup> of Ontario. The clays are of Mesozoic age and associated with sand deposits. Although they are reported to be of high quality, their remote location may hinder their commercial development.

*Stoneware Clays.*—Those employed for the better grades of stoneware are often at least of semirefractory nature, and of dense-burning quality.<sup>69</sup> They do not have to fire white. Such clays are found in part associated with the Carboniferous fire clays of the Central States, as well as in the Tertiary and Cretaceous formations of the East, South and West.

*Paving-brick and Sewer-pipe Clays and Shales.*—As a rule shales rather than clays are employed for this group of clay products. There is a large production from the Carboniferous shale formations of the Central States. Some of the Tertiary clays of Texas, California and Washington have also been used for this purpose. Some Carboniferous shale of Nova Scotia has been used for sewer pipe, and the clays of southwestern British Columbia have been similarly employed.

*Brick and Tile Clays.*—Practically none of the states are lacking in clays or shales that can be used in the manufacture of common brick.<sup>2,6-8,13,14,19,23,25,26,34,39,40,49-54,60,62-64,75,76,91,94</sup> The materials commonly used are red-burning surface clays of transported or residual types, and the clay sometimes selected is not of the best, especially if it is very sandy, as it makes a porous and weak brick. Probably the largest brickmaking district in the United States is that of the Hudson River Valley. Cream-burning calcareous clays are sometimes employed, not so much from choice as because they happen to be the common type of material in areas where such bricks are made, as around Mil-



waukeee, Wis.,<sup>52</sup> and some parts of Michigan.<sup>14</sup> Shales of Paleozoic age have been used to some extent in the Eastern and Central States.

In Canada<sup>29,30,60</sup> somewhat the same types of clay are used as in the United States. The surface clays are mostly red burning, but around Winnipeg, Man., cream-burning clays are common,<sup>60</sup> and therefore are selected. Silurian shales are used at Toronto, and Cretaceous shales in parts of Saskatchewan.

*Europe.*<sup>55</sup>—The most important clays of Europe are the kaolin deposits. Those at Cornwall, England, which have been worked for years and to depths of several hundred feet are widely used,<sup>40</sup> not only at home but abroad. They are the largest deposits of their type that have been developed anywhere. Also important are the kaolins of Karlsbad, Czechoslovakia, and those worked at several localities in Germany.<sup>79</sup> The English ball clays are well known to potters, and, like the Cornwall kaolins, have been exported to the United States in quantity. Belgium, Germany and England<sup>21,84</sup> all contain excellent deposits of fire clay. That from Gross Almerode, Germany, has been exported to the United States for glass-pot manufacture.

#### POLITICAL AND COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

It can hardly be said that control is much of a problem in the clay industry, because the United States is relatively independent of other countries for its supplies of raw clays, and only certain special kinds of high-grade clays have been imported. These have been gradually replaced by domestic materials except perhaps the highest grade of paper-coating clays.<sup>86</sup>

For many years there has been a somewhat steady importation of English kaolin or china clay for use in the manufacture of china, paper, paint, etc. The strong hold this product has had on the American market for years has probably been due in part to its more uniform character. Before the war more than two-thirds of the china clay consumed in the United States was imported from England, and as late as 1925, according to Bureau of Mines statistics, the imports were more than the domestic production. The replacement of foreign clays in the pottery and paper industry continued during the depression, and in 1934 the china-clay imports formed less than 20 per cent of the domestic consumption. This increase in the use of domestic materials has been due in part to their more careful preparation for the market.

In former years much English ball clay was imported, the potters in this country preferring it to the American material, which did not vitrify at quite as low a temperature; indeed, when the American ball clays were first developed some of the potters used to the English product were loath to class the domestic product as ball clay. In recent years, however, the domestic clay has replaced the imported ball clays and glass-pot clays.

Since the large majority of the clay-working plants in the United States obtain their supply of raw material from their own deposits, the production of this clay is not listed separately. According to Tyler<sup>96</sup> roughly 35 million tons of clay was produced in the United States in 1929, but its chief use was in the manufacture of heavy clay products. The figures of clay production issued formerly by the United States Geological

TABLE 10.—*Clay Sold by Producers in the United States, by Kinds<sup>a</sup>*

Year	Kaolin or China Clay and Paper Clay		Ball Clay		Slip Clay		Fire Clay	
	Short Tons	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value
1909-13 <sup>b</sup>	132,114	\$ 705,352	63,371	\$231,447	14,268	\$25,867	1,629,098	\$2,261,738
1925-29 <sup>b</sup>	453,618	3,834,825	116,127	890,457	6,839	37,000	2,810,001	7,747,918
1930.....	533,800	3,893,814	93,488	739,787	4,398	26,465	2,547,162	6,070,663
1931.....	443,300	2,946,953	83,007	639,798	1,916	13,613	1,473,161	3,741,038
1932.....	344,994	2,011,208	47,573	312,751	525	5,105	725,993	2,057,060
1933.....	411,233	2,366,339	64,551	400,564	1,562	11,365	1,133,693	3,141,545
1934.....	426,335	2,699,016	62,877	423,421	5,117	35,832	1,288,909	3,733,033
1935.....	523,585	3,766,109	90,469	607,730	4,316	25,839	1,783,321	4,532,565

Year	Stoneware Clay		Bentonite		Miscellaneous		Total	
	Short Tons	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value
1909-13 <sup>b</sup>	142,569	\$ 143,034			400,546	\$ 369,019	2,381,966	\$ 3,736,487
1925-29 <sup>b</sup>	88,575	188,055			568,869	1,220,458	4,044,029	13,918,173
1930.....	75,832	146,513	107,405	\$ 858,927	600,818	785,326	3,962,903	12,521,495
1931.....	57,466	131,915	78,815	472,045	381,830	406,823	2,519,495	8,352,185
1932.....	49,736	82,521	71,613	503,673	151,382	229,291	1,391,816	5,201,609
1933.....	28,188	59,581	117,428	760,174	83,518	101,049	1,840,173	6,840,617
1934.....	56,678	100,279	215,339	1,050,578	132,008	155,094	2,187,263	8,197,253
1935.....	35,460	70,280	189,840	1,071,412	168,913	216,490	2,795,924	10,290,425

<sup>a</sup> Minerals Yearbook, 1936, U. S. Bureau of Mines.

<sup>b</sup> Average.

<sup>c</sup> Up to 1930 bentonite was included under miscellaneous.

Survey and since 1923 by the United States Bureau of Mines represent chiefly clay that is sold to factories or firms on a royalty or tonnage basis. It consists mostly of high-grade clay used in the manufacture of white ware, refractories, or for filler in paper, paint or fabrics, and in some years is said not to have represented more than 10 per cent of all the clay mined. The figures of production do not include either clay used in manufacture of Portland cement, or that used for bleaching purposes, which is listed under "fuller's earth." It does include bentonite, which is used in part

for bleaching purposes as well as a variety of other uses, but not by itself for the manufacture of clay products. Even the fire clay reported does not include all of that type, as many refractories manufacturers operate their own deposits.

Table 10 gives the production and value of clays over a period of years.

It is interesting to note the rank of the five leading states, for production of each type of clay, as shown in Table 11.

TABLE 11.—*Clay-producing States in 1934, Arranged in Order of Rank*

Rank	Total Value	Total Tonnage	Kaolin and Paper Clay	Ball Clay	Fire Clay	Stoneware Clay
1	Georgia	Pennsylvania	Georgia	Kentucky	Pennsylvania	Pennsylvania
2	Pennsylvania	Georgia	South Carolina	Tennessee	Missouri	Ohio
3	Missouri	Missouri	Pennsylvania	New Jersey	Ohio	New Jersey
4	South Carolina	California	North Carolina		Kentucky	Washington
5	Kentucky	Ohio	Delaware		California	California

The reason for the reversed positions of Georgia and Pennsylvania in the first two columns is that the former state ranks first in value because of its output of sedimentary kaolin, while the latter is first in tonnage because of its large production of fire clay. In the fire-clay column, New Jersey would be only sixth. It produces considerable fire clay, but

TABLE 12.—*Salient Statistics of the Clay Industry in the United States, 1925-1929 and 1931-1934\**

Domestic Clay, Short Tons	1925-29 (Average)	1931	1932	1933	1934
Sold for:					
Pottery and stoneware.....	225,910	147,409	108,135	114,022	110,915
High-grade tile.....	74,350	96,632	44,329	32,101	26,310
Saggers, spurs, stilts, wads...	205,627	73,117	39,832	49,916	51,160
Architectural terra cotta.....	91,753	31,188	13,520	12,875	9,659
Paper.....	201,292	275,469	230,445	255,989	219,852
Rubber.....	31,996	34,501	33,719	49,615	48,259
Oilcloth and linoleum.....	11,885	7,411	5,326	6,715	9,061
Paints.....	18,047	12,920	7,983	10,859	11,869
Cement.....	70,913	121,196	50,281	22,747	24,581
Refractories.....	2,068,970	1,101,401	573,530	1,030,565	1,194,655
Miscellaneous.....	1,043,286	618,251	284,716	254,769	450,942
Total sold:					
Quantity.....	4,044,029	2,519,495	1,391,816	1,840,173	2,187,263
Value.....	\$13,918,173	\$8,352,185	\$5,201,609	\$6,840,617	\$8,197,253

\* Minerals Yearbook, 1934, U. S. Bureau of Mines.

much of it is mined by the manufacturer. The tonnage of Ohio stoneware clay happens to be greater than that of New Jersey, but the value is less.

It is also interesting to note the uses to which the different clays are put, and the relative amounts consumed.

The statistics in Table 12 indicate that since 1931 there has been a falling off in the amount of clay sold for every group of uses except in the paper and rubber industries. The demand for clay is governed in part by the conditions in the industries it supplies and in part by competition with substitutes.

There is naturally a close connection between fire clays and the iron and steel industries. In 1934, according to the U. S. Bureau of Mines, the demand for clays in the paper and rubber industries was increasing more rapidly than the industries themselves were. In the rubber industry this was due to the displacing of more costly materials by clay in

TABLE 13.—*Clay Imported for Consumption in the United States\**

Year	Kaolin or China Clay		Common Blue and Gross-Almerode Glass-pot Clay		All Other Clays				Total	
					Unwrought		Wrought			
	Short Tons	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value
1909-15 <sup>a</sup> .....	261,266	\$1,562,684	19,763	\$159,788	31,836	\$126,313	1,423	\$ 24,312	314,288	\$1,873,097
1925-29 <sup>b</sup> .....	339,014	3,055,885	12,150	113,307	57,001	493,983	4,047	52,550	412,192	3,715,725
1930.....	236,251	2,197,540	18,900	154,428	24,883	209,175	4,984 <sup>c</sup>	143,817 <sup>c</sup>	285,018 <sup>c</sup>	2,704,960 <sup>c</sup>
1931.....	151,426	1,056,393	15,183	116,446	15,615	125,326	8,376 <sup>c</sup>	237,859 <sup>c</sup>	190,600 <sup>c</sup>	1,536,024 <sup>c</sup>
1932.....	99,807	461,191	5,880	45,445	13,290	90,140	8,133 <sup>c</sup>	280,404 <sup>c</sup>	127,110 <sup>c</sup>	877,180 <sup>c</sup>
1933.....	116,180	632,437	7,099	69,639	17,623	141,992	9,756 <sup>c</sup>	336,435 <sup>c</sup>	150,658 <sup>c</sup>	1,180,503 <sup>c</sup>
1934.....	100,775	752,993	9,467	111,828	11,678	120,758	9,226 <sup>c</sup>	355,965 <sup>c</sup>	191,146 <sup>c</sup>	1,341,524 <sup>c</sup>
1935.....	125,963	959,821	15,552	165,560	24,488	220,382	7,453 <sup>c</sup>	289,828 <sup>c</sup>	173,456 <sup>c</sup>	1,635,591 <sup>c</sup>

\* Minerals Yearbook, 1936.

<sup>a</sup> Average.

<sup>c</sup> Includes "clays or earths, artificially activated with acid or other material," as follows: 1930 (June 18 to Dec. 31), 2,663 short tons valued at \$100,779; 1931, 4,912 tons, \$184,381; 1932, 7,328 tons, \$267,560; 1933, 5,640 tons, \$258,291; 1934, 3,867 tons, \$232,664; 1935, 3,589 tons, \$212,036; not separately classified prior to change in tariff.

the vulcanizing batch, but the opinion is expressed that this trend cannot continue indefinitely. In the paper industry the increased use of domestic clay is said to represent progressive displacement of foreign clays, brought about in part by better preparation of the native product. On the other hand, clay has to compete in the paper industry with other mineral products such as talc, pyrophyllite, gypsum, lime carbonate, et cetera.

*Imports and Exports.*—Table 13 shows the quantity and value of clay imported for consumption in the United States from 1909 through 1934. The classification there adopted is far from satisfactory, and yet it has been used for a number of years. The figures in the total column show

a marked drop in tonnage and value since 1930, most of which appears to be due to the falling off of kaolin imports. This, as explained elsewhere, is accounted for largely by replacement of English by American clay. The exports of domestic clays are given in Table 14.

TABLE 14.—*Domestic Clay Exported from the United States<sup>a</sup>*

Year	Fire Clay		All Other		Total	
	Short Tons	Value	Short Tons	Value	Short Tons	Value
1925-29 <sup>b</sup> ...	55,316	\$434,842	54,028	\$ 782,927	109,344	\$1,217,769
1930.....	62,660	519,788	73,870	1,108,586	136,530	1,628,374
1931.....	45,314	329,112	61,889	915,743	106,703	1,244,855
1932.....	22,086	228,073	59,273	826,550	81,359	1,054,623
1933.....	32,432	264,595	66,093	970,293	98,525	1,234,888
1934.....	36,053	308,424	84,264	1,147,555	120,317	1,455,979
1935.....	49,949	380,604	101,524	1,484,465	151,473	1,865,069

<sup>a</sup> Minerals Yearbook, 1936. Statistics of exports of clays were not separately recorded before 1916. High unit value indicates processed clays, mainly filtering and decolorizing clays or fuller's earth, mainly from Pacific ports.

<sup>b</sup> Average.

### PROSPECTING AND MINING

A knowledge of the geological characteristics of clay deposits is of considerable aid in prospecting for clays and in making a field examination. All natural exposures as well as artificial cuts should be carefully examined, not losing sight of the fact, however, that on slopes or steep surfaces there may be considerable weathering and sliding of the material, which covers up a portion of the material in place.

In unconsolidated deposits, a carpenter's auger attached to a sufficiently strong pipe may be used for boring the deposit. Such an outfit can be used to depths of 40 or 50 ft., but the system should be made in short sections, which can be connected by means of coupling. An auger outfit can also be used for horizontal boring. The data obtained from properly located boreholes can be used to determine both vertical and horizontal variations in the deposit. Where the ground is too hard to use augers, core drills may be employed.

If large samples are desired, test pits can be sunk in the deposit. Clay deposits are sometimes prospected by tunnels and shafts.

*Sampling.*—The Committee on Standards of the American Ceramic Society<sup>3</sup> recommends that for preliminary testing the body of clay shall be stripped of loose or foreign materials, and a series of straight, parallel trenches cut entirely across the outcrop. If the deposit is stratified and the beds dip, the trenches shall be cut across the dip. Each trench should be 12 in. wide and deep enough to yield 100 lb. of material. If natural outcrops are not available, preliminary trials may be made with a hand

auger, and test pits dug for further sampling. Should the deposit show beds that are visibly different from each other, they should be sampled separately. If preliminary tests show the deposit to be satisfactory, the deposit as a whole can be bored or drilled throughout its extent, spacing the holes not more than 100 ft. apart.

The samples collected from the different trenches are to be reduced to lumps not over 2 in. in diameter, mixed together, and reduced by quartering to 100 lb.

Too much stress cannot be laid on the fact that all samples collected should represent the average of the deposit or the bed. Furthermore, the clay should be carefully tested before a plant is erected. The writer has known of several plants erected on the site of improperly tested deposits; the result being failure of the enterprise.

Most clay deposits are worked as open pits, the method of excavation depending on the character of the clay, thickness and extent of beds, and character of the overburden. Where the deposit is small, or consists of beds of different quality, which it is desirable to separate, the clay may be dug by spades or mattocks. Selective mining of different beds is practiced in New Jersey, western Kentucky and Tennessee, and also in parts of California. Linton<sup>38</sup> states that in some California deposits over 20 ft. thick, beds as thin as 2 ft. may be separated in selective mining. With thicker beds, and a working face of not more than 20 ft. high, a steam shovel may be employed.

At some clay pits the face of clay, if not too high, may be undercut at the base, and wedges driven in at the top, thus causing a slice of the bank to fall and break up the clay, so that it can be more readily handled. If the clay deposit has a horizontal surface of some extent, it may be first loosened by plows, and the clay then gathered up by wheel or drag scrapers.

Shale banks are often blasted and the material that accumulates at the bottom gathered up by steam shovels. Occasionally shale is worked by a planer. This consists of a steel structure<sup>35,43</sup> carrying a power-driven steel chain provided with teeth, which scrape off pieces of shale. These pieces fall to the base of the face, and from there are carried by an endless belt to hoppers or vehicles. Such planers can cut a vertical or steeply sloping face. Depending on their construction, they can work on a straight line or cut a circular swath through an angle of 180°. A similar machine provided with small buckets has been used in soft clay.

For removal of overburden the methods used may be similar to those employed for excavating clay. In some places drag scrapers on cables are employed, or if the overburden is of sandy or gravelly character it can be removed by hydraulicking. At one shale bank near Seattle, Wash., where the stripping was 50 to 75 ft. thick, this method was used. The sale of the sand and gravel for concrete, etc., paid for the cost of stripping. The amount of overburden that can be economically stripped

depends on the thickness of the clay and its market value. Linton,<sup>35</sup> describing clay mining in California, states that the ratio of overburden thickness to that of clay varies from 1:1.2 to 1:1.75. In Tennessee as much as 35 ft. of overburden has been removed to dig 10 ft. of ball clay.

A unique type of mining is that employed in some of the North Carolina kaolin deposits. Circular pits 15 to 25 ft. in diameter, lined with cribbing, are sunk to the bottom of the deposit. The cribbing is fastened every few feet. When the clay is bottomed the cribbing is removed from the bottom up, and the pit is filled with stripping material. A more recent practice consists in using the large circular cribbed shafts as sumps into which the surrounding clay is washed by hydraulic jets. Bucket elevators raise the crude clay from the bottoms of the shafts, and discharge it into troughs leading to the washing plant. Hydraulicking is also used in the Cornwall district, England, where the pits may be 200 ft. deep or more.

In Florida the white clays have been excavated with a clamshell dredge floating in the pit. The material is dumped into barges or pumped ashore through large pipes to the washing plant.

Underground mining is commonly used only for extracting the better grades of bedded clay, and usually is carried out by the room-and-pillar method.<sup>27</sup> It has been extensively used in some of the fire-clay deposits in the coal measures of the Central and Appalachian States.

In Colorado, along the foothills, where the clay beds dip steeply, and are interbedded with sandstones, the beds are worked down the dip and along the strike, leaving pillars of the hard clay; timbers are also placed to hold the hanging wall.

The clay is hauled by different methods from the bank or mine to the stripping bins or manufacturing plant. At small pits, close to the plant, horse-drawn carts or small dump cars drawn by horse are often employed. For longer hauls, trains of cars hauled by electricity or steam are preferred. Where the mine opening is on a mountainside at some elevation above the valley, gravity planes or wire-rope trams may be used to bring the material down to the storage bins or plant.

Relatively few figures of cost have been published, and these are not always up to date. The following figures given by Tyler<sup>36</sup> were collected from several different sources:

In California the total costs for open-pit work ordinarily range between 20¢ and \$1.50 per ton. For mining alone the approximate figures are 10 to 20¢ a ton for scraper or power-shovel loading (up to \$1 if there is much hand sorting). Trimming out of the pit or carriage to a near-by bin costs 5 to 25¢ a ton, and incidental charges also range between 5 and 25¢ a ton. In eastern Canada, with wages at 27 to 40 or 50¢ an hour, total costs were 15.1 to 39.7¢ a ton for shale. Underground mining costs usually average higher, but they must be kept down to \$1 or less for mining, loading and sorting. The determining factor in every case is the cost per ton f.o.b. cars, which is only \$1 for certain cheap grades but ranges upward to \$5.50 for rarer varieties.

McMahon,<sup>43</sup> after making a careful study of clay-mining costs in the provinces of Ontario and Quebec, points out the difficulties in the way of obtaining accurate data.

### PREPARATION, TESTS AND SPECIFICATIONS

*Preparation.*—Clays used for the commoner grades of clay products and even for fire brick do not undergo much preparation, except the removal of pieces of stone. Even ball clays are not put through any purification before shipment.

Kaolins, because of their sandy character when mined, are commonly washed.<sup>25</sup> At the usual type of washing plant the crude kaolin, if not already disintegrated with water, may be dumped into a log washer, which breaks it up. From this the water and clay pass into a sand box, where the coarse sand settles and is continuously removed by a sand wheel. The water, with suspended clay, mica, and fine to medium sand, passes next into a series of troughs, which have a pitch of about 1 in. in 20 ft., and a total length of 500, or sometimes even 1000 ft. As the water flows through this troughing the sand and much of the mica settle, so that at the end little but clay is left in suspension. It then runs through a 100-mesh screen to the settling tanks. At some plants an alkaline salt like sodium hydroxide is added to the water to help to deflocculate the clay, a practice that may be particularly desirable if the clay contains much fine silt.

When the clay has settled in the tanks, the clear water is drawn off and the creamy mixture from the bottom of the vats is pumped out and into the filter presses. The filter cakes, containing about 25 per cent water, are dried by artificial or natural heat, then broken up.

Dorr classifiers have been used at some plants for washing the kaolin.<sup>61</sup> Air separation is used sometimes, and it is probable that it will find greater favor in the future.<sup>86</sup>

Weathering may improve the plasticity, and soluble salts may be brought to the surface and washed away; on the other hand, new ones may form, such as ferrous sulphate from pyrite in the clay.

Other forms of preparation are carried out at the factory after the clay has entered the manufacturing process, and need not be considered here.

*Tests.*—Tests of clay are made primarily to measure their physical properties, and certain tests have been recommended by the Committee on Standards of the American Ceramic Society,<sup>3</sup> which apply to clay to be used in its fired condition.

*Specifications.*—While no standard specifications have been recommended, it is always possible for the consumer to prepare them himself, indicating what properties the raw material shall possess.

*Plasticity.*—There is no standard test for determining the plasticity of a clay, although several different ones have been suggested.<sup>46, 57</sup> It is often determined by feel.



*Fineness.*—The fineness of clay may be tested by washing the sample through sieves and determining the weight remaining on each. Sieves are not fine enough to separate the smaller particles of clay, and for this purpose the hydrometer method, as used successfully by the U. S. Bureau of Public Roads, can be employed. Similar results are obtainable by the pipette method. The ordinary elutriator is not to be recommended, even though it has been much used in Europe.

*Water of Plasticity.*—This is determined by weighing the freshly molded test piece, air-drying, then again weighing after oven-drying at 110° C. The difference in weight is water of plasticity, which is calculated in percentage of the dry weight.

*Shrinkage.*—The drying volume shrinkage is determined by placing a molded test piece in kerosene in a volumeter, of which there are several kinds.<sup>46,57</sup> After drying, the piece is soaked in kerosene for 12 hr., then placed in the volumeter to determine its dry volume. The percentage of shrinkage can then be determined in terms of the dry volume.

The linear shrinkage can be calculated from the percentage of volume shrinkage by the formula

$$\text{Linear shrinkage} = \left[ 1 - \sqrt[3]{1 - \frac{b}{100}} \right] \times 100$$

in which  $b$  equals percentage of volume shrinkage. The linear shrinkage can also be determined by making a line of known length on the freshly molded test piece and measuring again when dried.

For shrinkage determinations of the fired pieces, the same methods are employed using water instead of kerosene in the volumeter.

*Shrinkage and Pore Water.*—The data obtained in determining volume shrinkage are employed here. Thus, for shrinkage water:

$$\frac{V_p - V_d}{W_d} \times 100$$

in which  $t_1$  = percentage of shrinkage water.

$V_p$  = plastic volume, c.c.

$V_d$  = dry volume, c.c.

$W_d$  = dry (100° C.) weight, grams.

Pore water is obtained from the formula

$$t_2 = T - t_1$$

in which  $t_2$  = percentage pore water.

$T$  = percentage of water of plasticity.

$t_1$  = percentage shrinkage water.

*Slaking Test.*—A 1-in. cube consisting of a mixture of 50 per cent clay; ground to pass a 30-mesh sieve, and 50 per cent potter's flint, is cut from a slab of the plastic material. This is dried in the room, then at 64° to

76° C., and finally at 110° C. It is cooled in a dessicator and then immersed in water on a  $2\frac{1}{2}$ -in. sieve. The time for it to disintegrate completely is noted.

*Transverse Strength.*—The plastic clay is molded into bars 7 in. long and 1 in. square. These are first carefully dried at room temperature, then at 64° to 76° and then at 110° C. They are cooled in a dessicator and broken in a machine in which they rest on supports 5 in. apart, the load being applied at the rate of about 100 lb. per minute. The modulus of rupture is calculated by the formula

$$MR = \frac{3Wl}{2bh^2}$$

when  $MR$  = modulus of rupture, lb. per sq. in.

$W$  = breaking load, lb.

$l$  = distance between knife-edges, in.

$b$  = breadth of bar, in.

$h$  = height of bar, in.

Since the clay shrinks in drying, the breadth and height of the bar must be measured before testing. Ten bars should be broken, and vary by not more than 15 per cent from the average.

*Firing Tests.*—Test pieces are fired over a range of temperature that depends on the type of clay, at a rate of 45° C. per hour up to a little below the point of drawing trials, and after that at a rate of 20° C. per hour. The fired trials are examined for color, hardness, shrinkage, porosity, etc. The fusibility is determined by grinding the clay to pass a No. 60 sieve, molding it into tetrahedra 30 mm. high and 7 mm. on a side at the base, and testing these in comparison with standard cones of similar size in a furnace with neutral or oxidizing atmosphere.

*Specific Gravity.*—The true specific gravity is determined in the usual manner in a pycnometer. The apparent specific gravity of a fired clay is determined by the formula

$$Ga = \frac{Wf}{Vf - (Sf - Wf)}$$

and the bulk specific gravity with

$$Gb = \frac{Wf}{Vf}$$

in which  $Wf$  = weight of fired piece, grams

$Vf$  = volume of fired piece, c.c.

$Sf$  = weight of saturated fired piece, grams.

*Absorption.*—For fired pieces this is determined by weighing the dry piece, soaking in water for 24 hr. then weighing again. The increase in weight is calculated in percentage terms of the dry weight.

*Apparent Porosity.*—This is calculated by means of the following formula

$$\text{Apparent porosity} = \frac{S_f - W_f}{V_f} \times 100$$

Saturation is obtained by soaking the test piece in distilled water at 20° C. for 100 hr., and boiling for 1 hr. during the first, twenty-fifth, forty-ninth and seventy-third hours.

### MARKETING AND USES

*Marketing.*—Producers of the cheaper types of clay products, such as building brick, drain tile and paving brick, or even common red earthenware, with hardly any exception, obtain their clay from their own deposits. Only the kaolins, slip clays, and many refractory clays, as a rule, are mined by separate companies or individuals and sold to the consumers by the ton.

Some clays and shales are sold on a royalty basis, this being quoted<sup>66</sup> as 5¢ a ton for common clays and shales, 10¢ for moderate-duty fire clay, and 10 to 25¢ for high-grade fire clays. The white-burning clays bring the highest prices on the market, but for any one type of clay the price may vary, depending on the amount of preparation it goes through before being shipped.

Refractory clays are rarely shipped long distances to market, unless by water, but china clays, because of their relative scarcity, will stand a longer haul. The two great whiteware-potting centers of the United States are Trenton, N. J., and East Liverpool, Ohio, but the nearest important domestic sources of white clay are western North Carolina, the Georgia-South Carolina belt, and Florida. The chief markets for these

TABLE 15.—*Prices of Various Clays in the United States, 1931–1934<sup>a</sup>*

	1934							
	1931		1932		1933		1934	
							January	December
China clay, f.o.b. mines South Carolina and Georgia:								
Crude lump No. 1.....	\$ 4.50-	\$ 5.00	\$ 3.50-	\$ 6.00	\$ 3.50-	\$ 4.00		
Crushed.....	6.00-	8.00	4.50-	6.90	4.50-	5.00	\$ 5.00-	\$ 6.00-
Air-floated:								
No. 1.....	9.00-	15.00	6.50-	15.00	6.50-	10.00		
No. 2.....	5.50-	8.00	5.50-	6.00	5.50-	8.00		
Florida, washed, crushed:								
Superwhite.....		12.50	11.75-	12.50	11.75-	12.75	12.75-	12.75
Superplastic.....		12.00	11.25-	12.00	11.75-	12.75	12.75	12.75
Delaware, No. 1.....	14.50-	15.00	13.00-	14.50		14.00	14.00-	14.00
English, f.o.b. United States								
port, lump, in bulk.....	15.00-	25.00	12.00-	21.00	14.00-	18.00	\$16.50-	\$25.00
							\$15.00-	\$22.00

<sup>a</sup> Metal and Mineral Markets quotations, from Minerals Yearbook, 1934, U. S. Bureau of Mines.

<sup>b</sup> Not quoted.

<sup>c</sup> Water-washed, \$1.50 per ton extra; in paper bags, \$2.50 extra.

clays are in the Central and Northeastern States, and this means an appreciable freight rate, the latter from Georgia being given as \$5.80 to Trenton and \$8 or \$9 to New England points.<sup>86</sup> English clays may have to pay a freight rate of about \$3.50 a ton, and duty of \$1.50 a ton, and American china clays have to meet this competition.

Table 15 gives the prices for domestic kaolins prepared in different ways, and Table 16 the average value per short ton of various kinds of clay over a period of years.

TABLE 16.—*Average Values per Short Ton of Various Kinds of Clay Sold by Producers in the United States<sup>a</sup>*

Year	Kaolin and Paper Clay		Ball Clay	Slip Clay	Fire Clay	Stoneware Clay	All Kinds of Clay
	United States	South Carolina					
1909-13 <sup>b</sup> .....	\$5.34	\$3.88	\$3.65	\$1.81	\$1.39	\$1.00	\$1.57
1925-29 <sup>b</sup> .....	8.45	8.93	7.67	5.41	2.76	2.12	3.44
1930.....	7.29	7.61	7.91	6.02	2.38	1.93	3.16
1931.....	6.65	6.84	7.71	7.10	2.54	2.30	3.32
1932.....	5.83	6.40	6.57	9.72	2.83	1.66	3.74
1933.....	5.75	5.99	6.21	7.28	2.77	2.11	3.72
1934.....	6.33	7.26	6.73	7.00	2.90	1.77	3.75
1935.....	7.19	7.57	6.72	5.99	2.54	1.98	3.68

<sup>a</sup> Minerals Yearbook, 1936.

<sup>b</sup> Average.

*Uses.*—Clays may be used in their unfired or fired condition. The properties that govern the use of clays in their raw condition are color, texture, bonding strength and adsorptive qualities. The uses to which unfired clays are put include the following:

Paper clays, usually kaolins of residual or sedimentary character. Whiteness, fineness and uniformity of texture are of prime importance. Somewhat similar clays are used as fillers in fabrics, and in ultramarine manufacture. This group may be designated as "fillers." The requisite properties of filler clays as specified by different consumers, either as groups or individuals, are somewhat conflicting, but whiteness and freedom from grit seem to be the essentials.<sup>89</sup>

Bleaching clays, employed in the decolorizing of mineral and organic oils, include some of the clays known as bentonites (see chapters VI and VII).

Bonding clays, which have strong bonding qualities, are widely used for binding together the sand grains in synthetic molding sands. Such clays are commonly tested when mixed with sand, the properties of strength and permeability being important. They are commonly fire clays, although bentonite is also much used for this purpose. Under this

head might also be included the clay used for making stabilized roads, in which is employed a properly proportioned mixture of gravel or crushed stone, sand and clay. The clay should be tested for its cohesiveness, and this is commonly done by the Atterberg test.<sup>57</sup>

In its fired condition, clay may be used for a variety of purposes, prominent among which are structural, refractory, decorative and household. The deciding factor is the physical behavior of the clay in both its raw and its fired condition. While different types of clay may be designated by certain names, such as china, brick, stoneware, terra cotta, etc., such terms refer only in a general way to their properties, and do not indicate restricted uses. Thus a clay suitable for brick might also be used for drain tile, or a paving-brick clay could also be used in sewer-pipe manufacture. Furthermore, many clay products other than the cheapest are often made of a mixture of clays, in order to get a material with suitable properties. Architectural terra cotta and chemical stoneware are usually made from a mixture of clays. Whiteware contains kaolin, ball clay, ground quartz and ground feldspar. Any reference to the uses of clay, therefore, might better be expressed in terms of physical properties than in terms of names. The following classification, given by Parmelee,<sup>47</sup> brings out these points.

### *Use Classification of Clays*

#### I. Clays burning white or cream, not calcareous.

##### A. Open-burning clays (i.e., still distinctly porous) at cone 15 (2606° F.).

Uses: If of good color or of good strength, is used for pottery. If of good or high degree of refractoriness, used for various refractories; if also of good color, used for special refractories (e.g., pots for melting optical glass).

1. Low strength. Type: residual kaolins of North Carolina.
2. Medium and high strength. Type: secondary kaolins of Florida and Georgia.

##### B. Dense burning (i.e., become nearly or completely nonporous) between cones 10 and 15 (2426° and 2606° F.). Medium to high strength, medium shrinkage.

###### a. Nonrefractory clays.

3. Good color. Uses: pottery, including certain whiteware, porcelains, stoneware.
4. Poor color. Uses: stoneware, terra cotta, abrasive wheels, zinc retorts, face brick, saggars.

###### b. Refractory clays.

5. Good color. Uses: refractories, especially for glass if they do not overburn seriously for five cones (about 1800° F.) higher. Also uses stated in 3.

##### C. Dense burning between cones 5 and 10 (2426° to 2606° F.) and do not overburn seriously at five cones (about 1800° F.) higher than the temperature at which minimum porosity is reached.

###### a. Nonrefractory clays, medium to high strength, medium shrinkage.

6. Good color; usually reach minimum porosity between cones 5 and 8 (2246° to 2354° F.). Type: ball clays. Uses: pottery, whiteware, porcelain and stoneware.
7. Poor color. Uses: stoneware, terra cotta, abrasive wheels, zinc retorts, face brick, saggars.

*b. Refractory clays.*

8. Dense burning at cone 5 (2246° F.); do not seriously overburn for 12 cones (about 432° F.) higher; highly refractory; softening point at cone 31 (3,182° F.) or higher; bonding strength minimum, 325 lb. per sq. in. Use: graphite crucibles for melting brass.
9. Dense burning at cone 8 (2354° F.); not overfiring at cones 13 or 14 (2550° F.). Strength and softening point as in 8. Use: steel crucibles.
10. Dense burning at cone 8 (2354° F.); not overfiring at cone 15 (2606° F.). Bonding strength, 250 lb. per sq. in. or higher. Softening point, cone 29 or higher. Use: glass pots.

**II. Buff-burning clay.**

*A. Refractory clays.*

- a. Open burning (5 per cent porosity or more) at cone 15 (2606° F.) or above.*  
Indurated. Nonplastic or slightly plastic (unless weathered). Type: flint clays.
  11. Alumina 40 per cent or less. Use: refractories.
  12. High alumina (over 40 per cent). Type: diaspore clays. Uses: refractories, abrasives.
- b. Open burning (5 per cent porosity or more) at cone 15 (2606° F.) but plastic.*
  13. Silica 65 per cent or less. Uses: firebrick and other refractories, terra cotta, sanitary ware, glazed and enameled brick.
  14. High silica (over 65 per cent). Type: many New Jersey fireclays. Uses: firebrick and other refractories.
- c. Dense burning (porosity under 5 per cent) between cones 10 and 15 (2426° to 2606° F.).*
  15. Medium to high strength, not overburning for five cones (about 1800° F.) higher than point of minimum porosity. Uses: glass pots, firebrick, saggars, and other refractories; architectural terra cotta, sanitary ware, enameled and face brick.
- d. Dense burning (porosity under 5 per cent) at cone 10 (2426° F.) or lower.*
  16. (See 8.) Uses: zinc retorts, firebrick, saggars and miscellaneous refrac-
  17. (See 9.) tories, architectural terra cotta, sanitary ware, enameled and
  18. (See 10.) face bricks.

*B. Nonrefractory clays.*

- a. Open burning (5 per cent porosity or more) at cones lower than 10 (2426° F.).*
  19. High or medium strength. Uses: architectural terra cotta, stoneware, yellow ware, face brick, sanitary ware.
  20. Low strength. Use: brick.
- b. Dense burning (porosity under 5 per cent) at cones lower than 10 (2426° F.).*
  21. High or medium strength. Uses: architectural terra cotta, stoneware, abrasive wheels, sanitary ware, face brick, paving brick.

**III. Clays burning red, brown, or other dark colors.**

- A. Open burning (do not attain low porosity at any temperature short of actual fusion).*
  22. Medium or high strength. Uses: brick, drain tile, hollow blocks, flower pots, pencil clays, ballast.
  23. Low strength. Use: brick.
- B. Dense-burning clays.*
  - a. Having a long vitrification range (5 cones or about 1800° F.).*
    24. High or medium strength. Uses: conduits, sewer pipe, paving brick, floor tiles or quarries, electrical porcelain, cooking ware, silo block, artware, face brick, architectural terra cotta, roofing tile.

25. Low strength. Uses: as dust body in manufacture of electrical porcelain, floor tile, building brick.

b. Having a short vitrification range:

26. High or medium strength. Uses: building brick, face brick, hollow block, flower pots.

c. Highly fusible, forming a glass at about cone 5 (2246° F.)

27. Slip clays.

IV. Clays burning light gray or light cream.

28. Containing calcium or magnesium carbonate or both. Never attain low porosity. Very short heat range. Use: common brick.

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## DIATOMITE

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**D**IATOMITE is a hydrous or opaline form of silica, commonly known as diatomaceous earth, diatomaceous silica, kieselguhr and, incorrectly, as infusorial earth. Obsolete locality or variety names such as bergmehl, desmid earth, white peat, randanite, polierschiefer, tellurine, tripolite and ceyssatite are no longer favored. Moler and Celite are trade names that have become associated respectively with Danish diatomites and those from Lompoc, Calif., and have been widely used in the technical literature.

## COMPOSITION AND PROPERTIES

*Chemical Composition.*—Diatomite is essentially hydrous silica (2 to 10 per cent combined water), but is frequently associated with organic matter (from traces up to over 30 per cent) and with varying amounts of inorganic impurities such as sand, crystalline silica, clay, volcanic ash, calcium carbonate, magnesia, soluble salts. In the natural or crude state, diatomite contains from 10 to 65 per cent or more of free water. Table 1 shows the wide range in chemical composition of diatomite samples from various deposits.

*Physical Properties.*—Pure varieties have low density and are friable, porous, chalklike masses, either stratified or massive; in color, usually white or light shades of gray, buff or green. Varieties containing organic matter range from oozes in lake bottoms to peatlike materials; impure varieties may be more or less claylike, sandy, calcareous or flinty.

Color: white, cream, gray, tan, brown, greenish to nearly black. Hardness: pure varieties easily friable and apparently soft 1 to 1.5 because of porosity, actual hardness of the microscopic particles 4.0 to 6.0. Specific gravity: 1.9 to 2.35. Apparent density (dry block form): 0.40 to 0.60 (25 to 37.5 lb. per cu. ft.). Apparent density (dry powder): 0.08 to 0.25 (5 to 16 lb. per cu. ft.). Crystal system: previously considered amorphous, but there is some evidence of faint crystallinity similar to high cristobalite.<sup>19,24,30,39,45</sup> Melting point: 1400° to 1750° C. Streak: white. Luster: dull to earthy. Cleavage: none. Fracture: parallel

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<sup>19</sup> References are at the end of the chapter.

with bedding planes, conchoidal or irregular. Transparency: opaque. Tenacity: crumbly to brittle. Solubility: insoluble in acids (except hydrofluoric), soluble in strong alkalis. Absorption: 1.5 to 3.5 times its weight of water. Index of refraction: 1.42 to 1.48. Thermal conductivity, block form (Celite): perpendicular to strata 0.79 B.t.u. per sq. ft. per hr. per in. thickness per  $1^{\circ}$  F. at  $1000^{\circ}$  F. mean; parallel to strata 1.13 B.t.u. per sq. ft. per hr. per in. thickness per  $1^{\circ}$  F. at  $1000^{\circ}$  F. mean. Thermal conductivity, powdered form (Sil-O-Cel, 16.0 lb. per cu. ft. density): 0.37 B.t.u. per sq. ft. per hr. per in. thickness per  $1^{\circ}$  F. at  $86^{\circ}$  F. mean; 0.73 B.t.u. per sq. ft. per hr. per in. thickness per  $1^{\circ}$  F. at  $1000^{\circ}$  F. mean.

TABLE 1.—*Chemical Analyses of Diatomaceous Earths from Different Localities, Moisture-free Basis*

Constituent	Lompoc, Calif.	Tlaxcala, Mexico	Mont- erey Co., Calif.	Los Angeles Co., Calif.	Mary- land	Vir- ginia	Ger- many	Algeria
Silica ( $\text{SiO}_2$ ).....	89.70	80.31	83.20	75.62	79.55	76.10	68.30	71.99
Alumina ( $\text{Al}_2\text{O}_3$ ).....	3.72	9.73	5.15	5.75	8.18	9.13	1.57	3.00
Iron oxide ( $\text{Fe}_2\text{O}_3$ ).....	1.09	2.80	1.58	2.56	2.62	2.56	2.37	1.12
Titanium oxide ( $\text{TiO}_2$ ).....	0.10	0.74	0.20	0.20	0.70	0.56	0.11	0.13
Manganese oxide ( $\text{Mn}_2\text{O}_3$ )....	0.02			0.05			0.09	
Lime ( $\text{CaO}$ ).....	0.35	0.18	1.30	3.	0.25	1.85	Trace	8.15
Magnesia ( $\text{MgO}$ ).....	0.65	0.53	1.41	1.50	1.30	1.65	0.18	2.30
Alkalies (as $\text{Na}_2\text{O}$ ).....	0.82	1.44	1.40	2.16	1.31	1.53	0.84	0.63
Ignition loss (combined water, CO <sub>2</sub> and organic matter)...	3.70	4.48	5.95	8.22	5.80	6.68	26.50	12.68
Total.....	100.15	100.21	100.19	99.86	99.71	100.06	99.96	100.00

*Microscopic Appearance.*—All diatomites consist of the siliceous remains of diatoms, in whole or partly fractured condition (sometimes associated with minor amounts of sponge residues, radiolaria, silicoflagellae, and other microscopic organisms, both plant and animal). There is an infinite variety in the types and conditions of diatom residues found, there having been identified some 8000 different species. The shape, size and structure of these vary enormously (Figs. 1 and 2).

#### ORIGIN AND MODE OF OCCURRENCE

Diatomite is of organic origin, consisting of the fossil remains of microscopic aquatic plants known as diatoms, of the order Bacillaria. These minute organisms thrive everywhere under suitable conditions of light, moisture and food supply. Each tiny plant is enclosed in a siliceous envelope, and when the organism dies it sinks to the bottom of the water, where the organic matter is more or less decomposed. The siliceous cases persist because of their imperishable nature, and thus form a deposit.

Diatoms grew in great profusion during various geological periods, particularly the Miocene, and the most important economic workings today are in the fossil deposits of this period. Some, however, are recent and others are in the course of formation now. Since diatoms live in fresh, marine and brackish waters, deposits of diatomite are likewise of corresponding origin. No large economic deposits are of earlier age



FIG. 1.—PROCESSED DIATOMACEOUS FILTER AID, JOHNS-MANVILLE CORPORATION.  $\times 200$ .  
FIG. 2.—FLORIDA DIATOMACEOUS EARTH (CALCINED).  $\times 200$ .

than the Tertiary. In the United States, there are deposits of both marine and fresh-water origin; in geologic age they range from the Cretaceous to the Recent.

The deposits near Lompoc, Calif., are of plankton marine origin and belong to the Monterey series of the upper Miocene. The main deposit today consists of 1400 ft. or more of stratified diatomite, now gently folded into a series of synclines and anticlines. The area of the Celite deposit is some 4000 acres. Deposits in Los Angeles and Monterey

Counties, California, are of different degrees of purity and of limited size. These are likewise marine Tertiary deposits, as are some undeveloped deposits in lower California.

There are a considerable number of fresh-water deposits in the Western States. All the known deposits of Oregon and Washington were laid down in fresh water in late Tertiary or Pleistocene times. They exist mainly as horizontal beds formed in prehistoric lakes. The numerous deposits of Nevada and some others of the Western States (Arizona, Utah, Idaho, New Mexico) also are of fresh-water origin. They occur as stratified basin-shaped beds, overlain and interlain with sedimentary and igneous formations.

Marine Tertiary deposits occur in Maryland and Virginia. The beds are intermixed and interstratified with sand and clay along the Potomac and Rappahanock Rivers and their tributaries. In New York, New Hampshire, the maritime provinces of Canada and Florida, there are recent deposits in ponds, peat bogs, marshes and small lakes.

The Algerian deposits are marine Miocene and occur in formations somewhat similar to those of the California coast regions. The French deposits are principally of fresh-water origin, having accumulated in Tertiary and Quaternary lake beds. Deposits in the Lausitz district, Germany, and those near Bilin, Czechoslovakia, are in an area of Tertiary basalt. The Lüneburger Heide deposits were formed in the last interglacial period and lie in water-soaked beds covered with soil and sand. The Danish deposits (late Tertiary) are of great thickness, intimately mixed with clay. They are often exposed in sea cliffs. Japanese deposits (Tertiary and Pleistocene) are small and basinlike.

The source of silica for the great diatomaceous deposits has been considered by numerous geologists. Since diatoms are aquatic plants, the silica to be utilized must be in solution or the organisms must have the capacity to extract silica from suspended silicates such as clay, etc. Plant physiologists investigating the role of silica in the lower plants are not in full agreement as to the manner by which the diatom obtains its silica and deposits it as the characteristically thin and highly ornamented membrane of opal. However, since nearly all natural waters contain some dissolved silica and it appears that diatoms have limited capacity at least to extract silica from suspended silicates, it is believed that these sources are sufficient to account for the growth of diatoms as found usually today and possibly also for some of the smaller diatomite deposits. It is doubtful, however, whether these sources could be adequate to explain the more extensive deposits, particularly of the Miocene period. It must be assumed, therefore, that when these great beds were laid down the waters contained relatively high concentrations of dissolved silica.

A relationship between volcanism and diatomaceous sediments was first advanced by Whitney,<sup>44</sup> who pointed out that silica in available form

could be supplied by volcanic agencies in the form of ashes, pumice, etc. Taliaferro<sup>40</sup> has elaborated this viewpoint and has associated the Miocene deposits with contemporary submarine volcanism.

### DISTRIBUTION OF DEPOSITS

Deposits of diatomite of varying degrees of purity and size are found rather widely but not extensively throughout the world. The most important deposit is near Lompoc, northern Santa Barbara County, California.

*United States.*—Deposits are found in many states, as follows: (1) California: in addition to those at Lompoc, there are deposits in Los Angeles County, near Covina and Torrance; in Monterey County, near Bradley and Monterey and in Shasta County, Pit River district (undeveloped). Minor occurrences are in Orange, Fresno, San Luis Obispo, Sonoma, Stanislaus and Lake Counties and on Santa Catalina Island; (2) Oregon: near Harper, Malheur County; Terrebonne, Deschutes County, and in Baker, Grant, Klamath, Wasco, Union, Crook, Lake and Wheeler Counties; (3) Washington: near Ellensburg, Kittitas County; in Grant County, Skagit County, and in Puget Sound districts; (4) Nevada: near Carlin, Elko County; Virginia City, Storey County; Lovelock, Humboldt County; Reno, Washoe County; Black Springs, Nye County; Lovelock, Churchill County; near Basalt, Esmeralda County, and in numerous other localities; (5) Arizona: in the San Pedro Valley, Graham County; near Mammoth, Pinal County and in the Bradshaw district, Yavapai County; (6) New Mexico: near Española, Santa Fe County and Rio Arriba County, and near Socorro, Socorro County; (7) Utah: in Utah, Box Elder and Beaver Counties; (8) Idaho: in Blaine, Owyhee and Washington Counties; (9) South Dakota: near Hermosa, Custer County; (10) Maryland: at Herring Bay, on the west side of Chesapeake Bay, Popes Creek, along the Patuxent River near Dunkirk and along Lyons Creek; (11) Virginia: commercially unimportant deposits at Richmond, along the Rappahanock River, in King George County and northwest of Petersburg, Dinwiddie County; (12) Florida: near Eustis and Clermont, Lake County, in Polk County and east of Pensacola; (13) New York: several localities in Herkimer County, in Suffolk County and near Cold Spring Harbor, Long Island; (14) Connecticut: near Stepney, Fairfield County; (15) Massachusetts: near South Framingham, Middlesex County; (16) Maine: near Blue Hill and Surry, Hancock County, and South Beddington, Washington County; (17) New Hampshire: pond deposits near Canaan, Grafton County; Center Ossipee, Carroll County; Laconia, Belknap County, and in Cheshire and Coos Counties; (18) Vermont: Caledonia County; (19) New Jersey: near Drakesville, Sussex County and in Morris County; (20) South Carolina: Williamsburg County;

(21) other states: localities have been reported in Nebraska, Alabama, Colorado, Delaware, Georgia, Montana and the Pribilof Islands, Alaska.

*Canada.*—Diatomite is found in British Columbia along the Fraser and Quesnel Rivers, at Prospect Lake near Victoria, and at other localities; in Nova Scotia, in Colchester, Cumberland and Pictou Counties. The principal deposits at present are near New Annan and on Digby neck. There are also deposits in the southern portion of New Brunswick, in Montcalm and Port Neuf Counties of Quebec and in the Muskoka region of Ontario. The deposits of Canada have been described in detail by Eardley-Wilmot.<sup>13</sup>

*Mexico.*—The principal deposit is in the state of Tlaxcala; others in states of Jalisco, Michoacan, Colima (Revillagigedo Islands) and Tepic (Las Tres Marias Islands).

*South America.*—Peru, near Arequipa; Chile, in the Atacama desert; in Tacna, Valparaíso and Nuble provinces and on Chiloe island; Brazil, Bahia and Minas Geraes.

*Europe.*—There are deposits of diatomite in Denmark, principally on the islands of Mors and Fur, lying in the Lim Fjord, also at Hollerup and Fredericia; in Germany, in the Vogelsburg, Hesse, between Altenschlirf and Steinfurt and in Lausitz, near Bilin, on the borders of Saxony and Czechoslovakia. The principal works are at Seifhennersdorf. Deposits also occur in Klieken, near Coswig, in Anhalt. The most important deposits occur in the Lüneburger Heide district, Hannover, where there are some 20 to 30 working pits in this area that may be classified into four producing areas: (1) Unterluss, Oberohe, Neuohe, Wiechel; (2) Munster; (3) Luhetal, along the upper Luhe valley, Bispingen, Hutzel, Steinbeck, Grevenhof, Schwindebeck; (4) Suderburg, Hamerstorf and Hösseringen. In France the present most important deposits are near Auxillac, north of Murat, Joursac, and Celles, all in the Department of Cantal. Other deposits, some of past importance, are in the Departments of Puy-de-Dôme, Haute-Loire, Ardèche and Aveyron. The active Auxillac quarries are in the upper Miocene; the older deposits in the Auvergne are principally Quaternary. Diatomite also occurs in: (1) Austria near Limberg; (2) South Bohemia, near Forbes (Borovany) and numerous other deposits; (3) Finland, lake deposits near Lavitaipole and Kymmene; (4) Hungary, near Zastreba; (5) Soviet Union near Pjatigorsk in Caucasian Mountains and Kreise Akhalych (Tiflis); (6) Georgia, District of Akhaltzik, near Kissatib and Saram; (7) Italy, near Santa Fiora, Bagnolo, Castel del Piano, between Tambolina and Metauro and in Tuscany south of Florenz at Monte Amiata; (8) northern Ireland, along the Bann River, in Londonderry and Antrim Counties; (9) Spain, in Province of Abacete, near Elche de la Sierra, also in the provinces of Castille, Seville and Cordoba; (10) Portugal, in the district of Samtarem. Norway, Sweden, and Yugoslavia have minor diatomite occurrences.



*Africa.*—Algeria, the principal deposits are in the province of Oran. The more important localities are: Saint Lucien near Saint Denis du Sig, Cassaigne, Ouillis and Pont du Chelif. Shipments are from Oran and Mostaganem. Deposits occur also in Kenya, Madagascar, Egypt, Nigeria, Union of South Africa.

*Japan.*—Numerous localities have been reported on the Island of Hokkaido (provinces of Shirabeshi, Kitami, Teshio and the Oshima peninsula); others on the Island of Kiushiu, prefectures of Kagoshima and Kumamoto and also on the small islands of Oki.

*Netherlands Indies.*—Diatomite occurs near Cheribon, in Java, and in Sumatra.

*Australia.*—Deposits are in Queensland, New South Wales, Victoria, Western Australia and Tasmania. New Zealand also has some occurrences. None of these have assumed commercial importance, except partly meeting local requirements. The deposits of Australia and New Zealand have been described rather fully in the literature.<sup>11,18,31</sup>

#### POLITICAL AND COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

It has been characteristic of the diatomite business that it has been developed and most requirements supplied by large individual companies or by trade organizations. Thus, in the United States, the Celite Company and the Johns-Manville Corporation pioneered the industry and continue to supply by far the greater tonnage for domestic consumption and also considerable tonnages for export shipments, particularly for filtration and filler uses. The International Diatomite Industries, Ltd., operating principally Nova Scotian deposits, is at present the leading company producing in Canada. In Germany the Vereinigte Deutsche Kieselguhrwerke G.m.b.H., Hamburg, has largely controlled the production and marketing of kieselguhr in that country. It represents a trade organization correlating the production of numerous works, principally in the Lüneburger Heide district. In France is La Société de Silices Fossiles de France, at Paris, which controls much of the Algerian diatomite. In Denmark, Moler Products, Ltd. and Molerindustri A/S largely control the industry. In Soviet Russia production and shipping is controlled by the Government. Private companies operate in north Ireland, Spain, Australia, Italy, Japan, etc. In the United States and Canada many minor companies and organizations have operated different deposits at different times. While most of these have been of temporary existence, with many ownership changes, some of the smaller producers have operated for many years and have been successful in specialties.

A feature of the diatomite industry in the United States has been a rather high degree of technical proficiency, not only in product and process development but also in its ability to develop new uses and to supply

technical service to the consuming industries. In North America, and to some extent elsewhere, the trade has come to expect distinct uniformity of grade and high-quality standards in diatomaceous products, except where it is used locally or when the lower quality products are utilized in the cheaper fields of building materials, ceramic insulations and concrete. The present developed United States resources appear adequate to meet all requirements for many years to come.

The first modern use of diatomite to any extent was in central Europe, particularly Bohemia, where it was employed principally as a polishing medium and as a clarifying agent in pharmacy. Beginning about 1860, with the development of the German deposits, came uses as an absorbent for nitroglycerin, as a source of silica for water glass, as a constituent of heat-insulating compositions and as a raw material for building materials. Later began the development of the Algerian, French, Italian and Danish deposits. In the United States small amounts of diatomaceous earth in small fresh-water deposits in the Eastern States, New England, New York, New Jersey, Maryland and Virginia were mined and used as an abrasive, filler and absorbent as early as 1850. The real development of the American diatomite industry began with the exploitation and operation of the deposit at Lompoc, Calif., about 1900. Production was very low until 1915, when financial backing was provided and, with a progressive management, the industry really began to develop. The field of filtration and development of efficient filter aids was pioneered (particularly for sugar refining) and the field of insulation was greatly broadened. High-temperature industrial insulation may be stated to have begun with the application of diatomite for these purposes on a sound technical basis, and the requirements of government and industry during the war period aided the new industry materially. Production increased steadily and in some products rapidly, reaching a maximum in 1929. During the period of economic depression, production of diatomite fell off, particularly for insulations and building materials. In the direct consumption industries, such as sugar refining, filtration generally, and in many filler uses, the demand for diatomaceous products held up comparatively well in the United States and throughout the world.

Published production statistics for diatomite have been incomplete and somewhat confusing. Early figures are particularly unsatisfactory. Since the figures that have been compiled may be obtained from government publications and other books readily accessible,<sup>5,11,13,31</sup> they will not be duplicated here in further detail. Production in the United States since 1921, in three-year periods, is shown in Table 2. World production figures for diatomite are given in the Imperial Institute and United States Government publications and annually in *The Mineral Industry* (McGraw-Hill Book Co., New York). Today, the principal producing nations are the United States, Germany, Denmark, Soviet Republic,

Algeria, Japan (including Chosen), and France. Not unimportant quantities are produced in North Ireland, Spain, Australia, Canada, Italy and Hungary. Minor producers are Norway, Sweden, Chile, Netherlands Indies, Mexico, Portugal.

TABLE 2.—*Production of Diatomite in the United States*

Years	In Three-year Period, Short Tons	Average per Year, Short Tons
1921-1923	162,768	54,256 <sup>a</sup>
1924-1926	219,331	73,110 <sup>a</sup>
1927-1929	286,426	95,475 <sup>b</sup>
1930-1932	248,273	82,758 <sup>b</sup>
1933-1935	244,342	81,447 <sup>b</sup>

<sup>a</sup> From *The Mineral Industry of the British Empire and Foreign Countries—Diatomaceous Earth*. Imperial Institute. His Majesty's Printing Office, London, 1928.

<sup>b</sup> From *Minerals Yearbook, 1935*. U. S. Bur. Mines. Government Printing Office, Washington, 1935.

The greatest diatomite resources, undeveloped or in reserve, are in the United States, Denmark, the Soviet Republic, Japan and Chosen, Algeria, Germany, Kenya (unproved) and, to a minor extent, Canada. Of all these, the greatest quantity of good quality material is distinctly in the United States. Only totally unimportant quantities of the best quality filter and filler material have come from Denmark, Soviet Republic, Japan or Algeria. The chief importing nations at present are the United Kingdom (Australia, England, Ireland, India), Canada, France, Norway, Poland, Cuba, Peru, Italy, Yugoslavia, Argentina, Java, Japan. Important aspects of diatomite production since 1935 are as follows: (1) leading position maintained by United States; (2) some revival of German industry (although believed not to have equaled production prior to 1930); (3) decrease in Algerian production and export, owing to economic conditions in France and the value of the franc; (4) increase in production in Soviet Russia, including Georgia, in Japan and north Ireland.

The outlook for the immediate future is considered favorable. With more stable economic conditions, world production may be expected to exceed 200,000 tons annually, with United States production passing 100,000 tons. With further development of uses and lowering of prices, total production may be expected to increase steadily for some decades. There is, however, no immediate expectation of revolutionary advances that would boost production unusually rapidly.

#### PROSPECTING, EXPLORATION AND MINING

In the dry, compact, stratified deposits, samples may be obtained from the surface outcrops and examined microscopically, physically or chemically. The purer beds are thus determined and further prospecting

results. Diatomite lends itself to core drilling readily and in some places prospecting is done in this manner. In others, trenches, tunnels, and vertical shafts of narrow cross sections are used to examine the diatomite away from surface conditions of alteration and leaching. These are more satisfactory methods of examination because of the ease with which the diatomite can be excavated. The openings permit a careful examination of the appearance of the material, its stratification, compactness, and inclination of beds. In the wet bog, lake, or swamp deposits, auger drills are often used, so that one foot of material can be brought up at a time. For under-water sampling, a casing is driven into the mud and boring is done inside the pipe. Tonnages are based on the amount of dry material in a cubic foot of the earth.

Where the diatomite is compact, the usual practice in the United States is to quarry on the surface with gasoline, steam, or Diesel shovels, and dragline hoists. In some locations, underground methods are employed, using simple shrinkage or room-and-pillar stoping. In most western United States deposits, the diatomite requires little or no timbering if pillars are left to support the roof. At Lompoc, Calif., gasoline and Diesel shovels load diatomite in the quarries into large dump trucks, which haul to vertical storage shafts. A 9500-ft. tunnel is electrified for underground hauling to the milling plants.

In eastern Canada and northeastern United States the diatomite is recovered from bogs, lakes and swamps. Here the diatomite is mined by dredging or by preliminary draining. After draining of water, recovery is by hand shoveling into dump cars, by bucket dredges, or by suction dredges. The wet diatomite is piled up to drain off free water, then spread out to air-dry before treatment.

#### PREPARATION FOR MARKET, TESTS AND SPECIFICATIONS

The method of preparation for market depends on the mode of occurrence, composition, and uses intended. In Denmark the impure, clayey material is simply milled and used for fabrication of ceramic articles (industrial and building). When it occurs in recent deposits, as in peat bogs, ponds, etc., the material is dredged, classified, dried and calcined (as in New York State and Florida). When coming from pits, as in the Lüneberger Heide, the material is dug, mostly by hand, calcined in lump form (or in special furnaces), elutriated, classified, et cetera.

In the western United States deposits, the crude earth from open quarries, cuts, etc., is field dried to some extent and then transported for milling. The large producers, however, have equipment and processes for drying or for drying and milling simultaneously. Diatomite products may be classified broadly as brick or block, crushed aggregates and pulverulent powders. Diatomite brick, with clay or other binders and with or without organic filler to be burned out, are fabricated with

conventional equipment: blending bins, puggers, presses, driers, kilns, sizing equipment, etc. The principal manufacture of brick and pressed block is in the United States, England, Germany and Austria. Aggregates are prepared by crushing, screening, and grading—all with more or less conventional equipment.

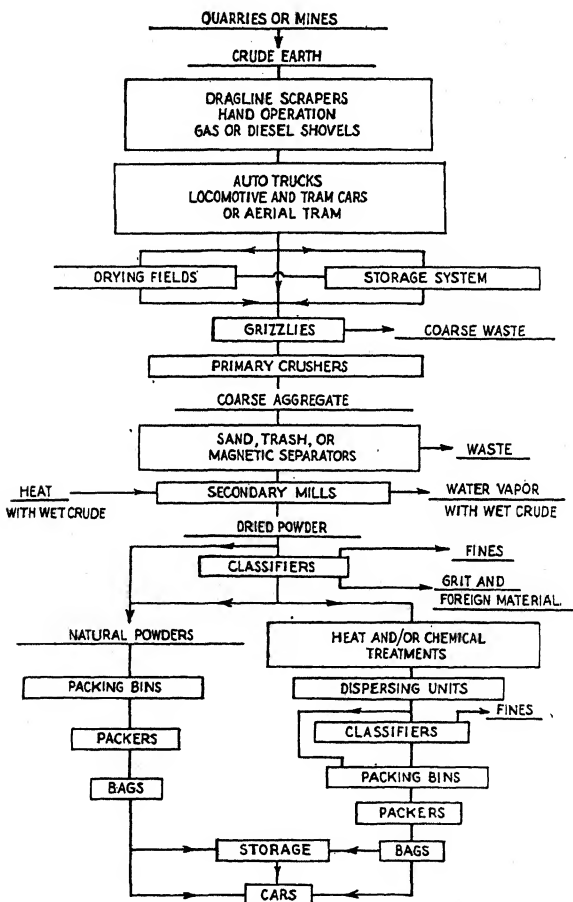


FIG. 3.—FLOWSHEET FOR DIATOMITES FROM DEPOSITS IN WESTERN UNITED STATES.

In the preparation of diatomaceous powders, the crude (field dried or wet) is conveyed to storage system or directly to trommel screens or grizzlies, then to primary crushers, mechanical traps for removal of rock, trash, flint or coarse impurities of any kind, thence to driers or to the secondary mills in combination with driers, thence to air classifiers for removal of finer grit and foreign matter and sometimes to classify pneumatically according to particle size. Many types of primary crushers may be employed. For secondary milling, mills on the swing-

hammer principle or centrifugal fans are preferred. Some products are calcined and chemically treated; the dried powders go to rotary or stationery kilns or to treatment tanks. Following either heat or chemical treatment, final dispersion of the powders is generally necessary and this is accomplished by special mills or blowers. In some instances, further purification and classification is effected pneumatically, subsequent to calcination. Water classification is carried out to some extent in Germany.

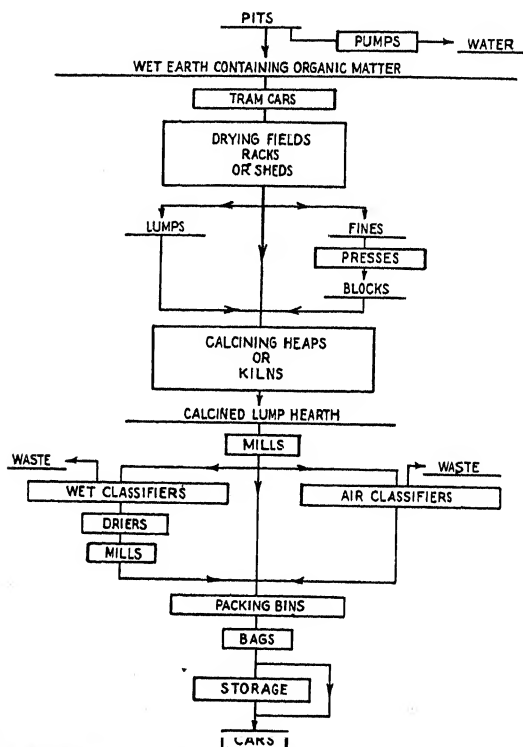


FIG. 4.—FLOWSHEET FOR DIATOMITE FROM PIT MINING, EUROPEAN PRACTICE.

Three idealized and simplified flowsheets are shown herewith for different methods of processing raw diatomite (Figs. 3 to 5).

*Tests and Specifications.*—Crude diatomite is evaluated on the following properties: freedom from impurities (sand, volcanic ash, crystalline silica, organic matter, clay, lime, soluble salts, etc.); microscopic structure (types of diatom forms and their condition, whole or broken, and relative proportions of different diatom forms, presence or absence of exceedingly fine particles); apparent or bulk density; friability (behavior on milling); color; opaline silica content.

The value of diatomaceous products is determined by: microscopic structure, bulk density (loose, tamped or on vibration); absorptive capac-

ity (water, oil or other liquids); chemical composition (iron, alumina, manganese, rare metals, alkalis, organic matter, etc.); specific gravity (care required for high accuracy); screen analysis (usually wet screening for finer than 30 mesh); particle size (generally by sedimentation methods); color (dry and in water, oils, etc.); conductivity thermal (standard methods); moisture (free); combined water (loss on ignition, in absence of organic matter and carbonate); special tests such as filtering efficiency and workability as admixture.

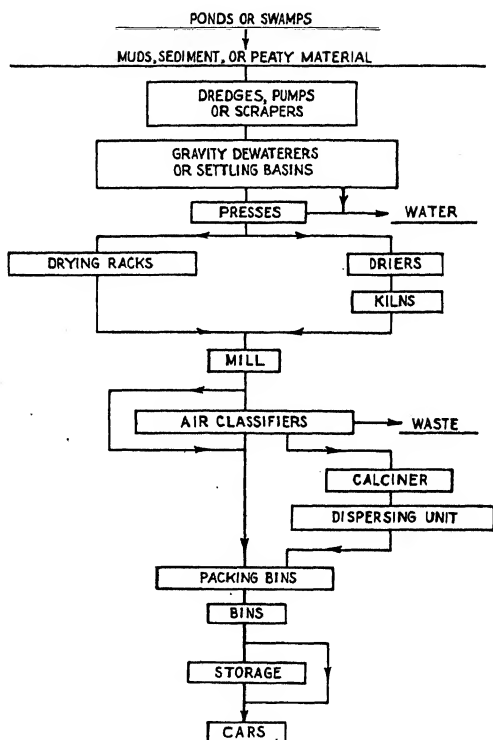


FIG. 5.—FLOWSHEET FOR POND OR BOG DEPOSITS, EASTERN UNITED STATES.

Specifications for diatomaceous products vary greatly because of the wide diversity of uses and requirements. For low-priced crude near sources of supply, the only requirements are bulk density and moisture content. For some specialized filtration and filler uses, definite chemical and particle-size specifications are required. For some polish and abrasive uses there are exacting requirements for mesh size and freedom from grit. For some filler uses there are equally stringent requirements for color and particle size. Many customers have set up special requirements that are not publicized. There are several government specifications, particularly for insulating materials, admixtures and fillers. The

principal producers have also supplied specifications for many of their standard products. It is frequent practice to submit standard samples in lieu of written specifications, and for many diatomaceous products this is recognized as good practice.

It is beyond the scope of this article to give detailed specifications for diatomaceous products. The following may serve as guides in indicating the properties considered most important for different general uses. Insulating compositions: apparent density (brick, block, etc.); bulk density (aggregates and powder); microscopic structure; mesh or screen analysis (aggregates, granules and powders); thermal conductivity; moisture. Filter powders: microscopic structure and particle size; chemical purity and inertness; low density; filter performance. Fillers: chemical purity and inertness; particle size and microscopic structure; fineness and freedom from grit; color; absorptive capacity. Admixtures: reactive silica; chemical composition; fineness; workability.

#### MARKETING, USES AND PRICE

*Marketing.*—The important sources of diatomite are generally distant from the principal markets. Furthermore, the material is bulky, both factors contributing to high freight charges. Packaging costs also are high, for care is required in packing and shipping because of the fragile nature of brick and possible injury to the structure of powders. Diatomite materials are rarely shipped in bulk, although crude may be so handled. The greater tonnage of diatomaceous products is purchased in carload quantities.

Marketing problems and the development of uses in the United States have been largely promoted by the pioneer and largest producer, first the Kieselguhr Company of America, then the Celite Company, and now the Johns-Manville Corporation. The policy of these organizations consistently has been one of progressive research and development (process, product, and uses). The uses of diatomaceous silica, in order of approximate importance, may be classified broadly as follows: filtration, insulations, fillers and miscellaneous, and admixtures. It is not possible here to do more than list some of the very extensive applications and uses.

*Filtration.*—Raw cane-sugar manufacture, cane-sugar refining, beet-sugar manufacture, molasses, corn sugar and glucose, maple sirup, beer, wines, distilled spirits and liquors, fruit juices and beverages (grape, prune, cider, citrus), malt products and extracts, water, dry cleaning, mineral oils and petroleum products (dehydrating, emulsion breaking, refining, filtration, dewaxing, sludges, tars), vegetable oils (cottonseed, peanut, linseed, corn, castor, coconut), animal oils and fats (fish oil, lard), liquid soaps, gelatin, glue and adhesives (vegetable and animal), chemical solutions, salts and salines, metallurgical slimes and



solutions, sewage, gas purification, pyroxylin and cellulose acetate, varnishes and lacquers, trade wastes and effluents, rigid filters (bacterial etc.), porous diaphragms, separators, etc., flavoring extracts, vinegar, hydrogenated oils, alginates, starch pastes, sizing, etc., dyestuffs, used crankcase oils, analytical and laboratory uses, serums and antitoxins, perfumes, extracts, pharmaceuticals and cosmetics, vitamin extracts, et cetera.

*Insulations.*—Diatomite in its various forms is widely used for industrial heat and cold insulations: power-plant equipment, in steel and nonferrous metallurgy and heat-treating, petroleum refineries, glass manufacture, ceramic kilns and equipment, gas-generating equipment, ovens, furnaces, kilns, pipe-covering, refrigerators, cold-storage buildings, metal-annealing, etc. The common types of products used are block, brick and slabs, aggregates, powders and cements. Brick may be "natural" as cut from the deposit or fabricated with or without inorganic binders and with or without additional porosity as by burning or melting out organic matter. Block and pipe-covering are molded with bonding agents, fiber, magnesia, etc. Cast compositions are made with aggregate or powder and a hydraulic bonding agent such as cement, gypsum magnesia, etc. Mortars, cements, etc., are made up with bonding agents, fiber, etc., and usually mixed with water and applied on the job. For metal-annealing, powder is generally employed. For cold-storage warehouses and low-temperature insulations, block, aggregate or powder is commonly used. In building and home insulation for both heat and sound, powder, granules, blocks, sheets, etc., are standard forms.

*Fillers.*—Absorbent for acetylene, battery-box compositions, molded asphaltic compositions, roofing, flooring, waxes, paints, varnishes, lacquers, pigments, catalyst support (hydrogenation of vegetable oils, coal and oil shale), oxidation and vapor-phase reactions, fuses and explosive caps, rubber, match-head compositions, natural and synthetic plastics, sulphur, dynamite and other explosives (liquid oxygen, etc.), polishes (silver, metal, automobile, cake, liquid, paste), carrier for chemical reactions, fire-resistant compositions, absorbents, insecticide carriers, paper (wallpaper, blotting, filter, glassine, printing, pitch control), abrasives (glass, dental, cleansing compositions), absorbent for radioactive emanations, safe filler, linoleum, artificial leather, sealing wax, glue, artificial stones, pharmaceuticals and cosmetics, putties, packings, etc., to prevent caking and hardening, mold wash, soaps, phonograph records, printing inks, absorbents for disinfectants, drying agent, fertilizers.

*Miscellaneous.*—Manufacture of water glass and soluble silicates, manufacture of ultramarine, manufacture of glazes, enamels, etc., fine reactive silica for chemical processes, manufacture of oil-decolorizing products and synthetic silicates.

*Building Industry.*—Admixture for concrete, mortars and cements; constituent of high-silica cements and puzzolan cements; flooring, pave-

ments, roads, roofing, light-weight building brick, block slabs, etc., wall-board, panels.

*Price.*—Prices for diatomaceous products have remained reasonably constant since 1918, when the increase in production costs due to war conditions was pronounced. The increased costs of fuel, labor and equipment during the period 1920 to 1930 were offset to some extent largely by process improvements and increased operations of the major producers. Cost trends were somewhat lower beginning in 1931. Detailed costs for diatomaceous earth are somewhat difficult to give, since the price range is rather broad, depending on the source of the earth and the processing necessary to prepare it for market. Crude diatomite at the deposits in Denmark, Soviet Russia, Algeria, and in western United States is cheap, \$5 per ton or less, upward. Standard products, admixtures, insulation and filtration grades range in price from \$10 to \$40 per ton at the mines. For highly purified or selected specialty grades, the prices come to \$100 per ton or higher. Insulating brick manufactured in the United States range in price from \$40 to \$80 per thousand at shipping point. Prices for kieselguhr have been listed in *Chemical and Metallurgical Engineering* as follows: 1921–1922, \$61 per ton; 1923–1934, \$50 to \$55 per ton.

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## FELDSPAR

By B. C. BURGESS,\* MEMBER A.I.M.E.

**F**ELDSPAR is the commonest mineral in the crystalline rocks. It is usually in small grains intimately associated with other minerals. Commercially, feldspar is obtained only from pegmatites. According to Hess,<sup>21</sup> "The pegmatites are undoubtedly the most bizarre, the most contradictory, the most complex and altogether the most interesting group of rocks known."

## COMPOSITION AND PROPERTIES

The feldspars form a group of which the principal species are orthoclase, microcline, albite and anorthite. These are aluminum silicates of potassium, sodium and calcium. There are also a barium feldspar, celsian, and barium orthoclase feldspar, hyalophane, rarely found and of no commercial importance. None of the minerals in the feldspar group are found pure or nearly pure. The potash feldspars, orthoclase and microcline, always contain some albite (soda orthoclase and soda microcline, anorthoclase). In turn, the soda feldspars always contain some anorthite (lime feldspar). (There is a series of soda-lime feldspars known as plagioclase in which the albite and anorthite molecules replace each other in varying proportions from albite through oligoclase, andesine, labradorite, and bytownite to anorthite. Chemical composition of the principal feldspars is given in Table 1.

Commercial feldspars, in addition to being intergrowths of at least two species of feldspar, always contain one or more of the accessory minerals, such as quartz, muscovite, biotite, garnet and tourmaline, as well as small but varying proportions of the decomposition product, kaolinite. An intergrowth of quartz and feldspar is frequently found containing about 75 per cent feldspar and 25 per cent quartz. The quartz is often distributed through the feldspar uniformly and appears in parallel lines of wedge-shaped grains. This is referred to in the literature as "graphic granite" or *schriftgranit*, and by the miners is called "corduroy" spar.

Perthite is an interlamination of orthoclase and albite. Originally, the name was applied to the mineral from Perth, Ontario, but now it is in

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<sup>21</sup> References are at the end of the chapter.

general use in the adjective form, "perthitic" intergrowth. All commercial potash feldspars are perthitic. Cornwall stone is a feldspar-quartz-kaolinite product obtained from a semikaolinized deposit in England. A similar product from North Carolina is marketed as Carolina stone.

TABLE 1.—*Composition and Properties of Principal Feldspars*

Mineral	Orthoclase	Microcline	Albite	Anorthite
Formula	$\text{KAISi}_3\text{O}_8$	$\text{KAISi}_3\text{O}_8$	$\text{NaAlSi}_3\text{O}_8$	$\text{CaAl}_2\text{Si}_2\text{O}_8$
CHEMICAL COMPOSITION, THEORETICAL PER CENT				
$\text{SiO}_2$ .....	64.7	64.7	68.7	43.2
$\text{Al}_2\text{O}_3$ .....	18.4	18.4	19.5	36.7
$\text{CaO}$ .....				20.1
$\text{K}_2\text{O}$ .....	16.9	16.9		
$\text{Na}_2\text{O}$ .....			11.8	
PHYSICAL PROPERTIES				
Crystal System	Monoclinic	Triclinic	Triclinic	Triclinic
Refractive index.....	1.524	1.526	1.529	1.584
Specific gravity.....	2.56	2.56	2.605	2.765
Melting point, deg. C.....	1200	1200	1110	1532

*Properties.*—The crystals of the different species are similar in angle, in general habit (Table 1) and in methods of twinning. The prismatic angles are nearly  $60^\circ$  and  $120^\circ$ . The cleavage is good in two directions at  $90^\circ$ , or nearly  $90^\circ$ . The luster is vitreous to pearly (subvitreous to dull in altered varieties). The streak is white. The fracture is uneven. Colors are generally white, cream and pink, also milky, clear, buff, brown, red, gray, green and bluish. Hardness is 6 to 6.5.

#### ORIGIN, MODE OF OCCURRENCE AND DISTRIBUTION

According to Clarke,<sup>16</sup> the feldspars constitute 59.5 per cent of the igneous rocks, quartz being the next most abundant single mineral at 12 per cent. The hornblende-pyroxene (ferromagnesian) group comprises 16.8 per cent of the average.

Pegmatites, the chief source of feldspar, vary greatly in mineral composition, but as sources of commercial feldspar the "granite" type, consisting essentially of feldspar, quartz and mica, predominates. A second type, according to Bastin,<sup>6</sup> classified as "soda" pegmatite, contains no quartz, no tourmaline, and little or no mica, but consists mainly of albite with small quantities of hornblende. Pegmatites are emanations from granitic magmas that have solidified in dike-like bodies in the enclosed

rocks. Their formation has probably been a long continuing process in which hydrothermal replacement followed the original magmatic injection. They are found in schists, gneisses, granite, diorite and other deep-seated rocks. However, a few pegmatites are found in limestone and other sedimentary rocks. As a natural consequence of such a mode of origin, pegmatites are characterized by extreme irregularity in size and shape of the deposits, size and distribution of the essential minerals, and number and proportion of the accessory minerals. According to

TABLE 2.—*Analyses and Calculated Mineral Content of Commercial Feldspars of the United States and Canada*

PERCENTAGES

No.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Loss	Potash Feldspar	Soda Feldspar	Lime Feldspar	Quartz	Other Minerals	Source
1	67.0	18.5	0.07	0.3	T	11.8	2.0	0.3	69.9	17.0	1.5	5.9	5.7	North Carolina
2	67.5	18.3	0.05	0.5	T	10.3	3.0	0.3	61.0	25.4	2.5	8.0	3.1	
3	68.8	17.8	0.1	0.5	T	9.5	3.0	0.3	56.3	25.4	2.5	11.2	4.6	
4	69.5	17.5	0.1	0.8	T	8.1	3.6	0.3	47.9	30.6	4.0	14.1	3.4	
5	73.5	15.3	0.1	0.5	T	7.3	3.0	0.3	43.2	25.4	2.5	25.2	3.7	
6	69.0	18.2	0.1	1.3	T	5.5	5.5	0.3	32.4	46.6	6.5	13.2	1.3	
7	70.0	18.1	0.1	1.5	T	3.5	6.5	0.3	20.7	55.2	7.5	15.7	0.9	
8	67.3	18.5	0.05	0.5	T	11.0	2.6	0.3	65.1	22.0	2.5	7.1	3.3	Virginia
9	69.1	17.5	0.1	1.0	T	9.0	3.2	0.2	53.3	27.2	5.0	12.8	1.7	
10	67.6	18.1	0.1	0.3	T	11.3	2.3	0.2	67.0	19.5	1.5	8.4	3.6	New York
11	74.6	15.3	0.13	1.0	T	2.8	5.8	0.3	16.6	49.3	5.0	26.7	2.4	
12	65.4	19.6	0.1	0.2	T	11.3	3.4	0.2	67.0	28.8	1.0	0.4	2.8	New England
13	67.8	18.4	0.1	0.3	T	10.0	3.0	0.3	59.2	25.4	1.5	8.8	5.1	
14	71.3	16.1	0.1	0.2	T	9.4	2.9	0.2	55.6	24.6	1.0	17.0	1.8	
15	74.0	14.8	0.1	0.3	T	8.1	2.6	0.2	47.9	22.0	1.5	25.8	2.8	Canada
16	65.1	19.5	0.15	0.4	T	13.1	1.7	0.2	77.5	14.4	2.0	1.8	4.3	
17	65.5	18.7	0.1	0.4	T	12.8	2.3	0.2	75.7	19.5	2.0	1.2	1.6	
18	65.7	19.6	0.1	0.7	T	10.6	2.9	0.3	62.7	24.6	3.5	4.0	5.2	Maryland
19	68.2	19.6	0.1	0.7	T	2.1	9.1	0.3	12.4	77.2	3.5	4.3	2.6	
20	64.7	19.7	0.04	0.3	T	12.2	2.8	0.4	72.2	23.8	1.5	0.0	2.5	
21	66.3	19.4	0.13	0.7	T	9.5	3.6	0.3	56.3	30.6	3.5	5.1	4.5	Colorado
22	65.8	18.8	0.04	0.3	T	11.8	3.1	0.3	69.8	26.3	1.5	1.4	1.0	Minnesota
23	65.1	19.7	0.04	0.3	T	12.2	2.4	0.3	72.2	20.4	1.5	1.3	4.6	Arizona
24	66.1	19.2	0.1	0.4	0.2	10.7	3.3	0.2	63.4	28.0	2.0	3.3	3.3	California

Schaller,<sup>33</sup> the general sequence of mineral formation in a pegmatite is somewhat as follows: high-temperature potassium feldspar, inversion to microcline, a little perthite, quartz, albite, muscovite, and the general group of such minerals as black tourmaline, garnets and beryl, followed by the lithium minerals, the phosphates, sulphides, carbonates and oxides.

The kaolin content of all commercial feldspars is a result of the natural processes of rock decomposition. Surface weathering undoubtedly is the cause of kaolinization of the feldspars of the Southern Appa-

lachian region of the United States. The kaolin in Cornwall stone may be the result of pneumatolytic action. Carbonic and humus acids are known to be effective agents in the kaolinization of feldspar. Sericitization often accompanies kaolinization. Either or both are often accompanied by solution of iron-bearing minerals, which stain the feldspar.

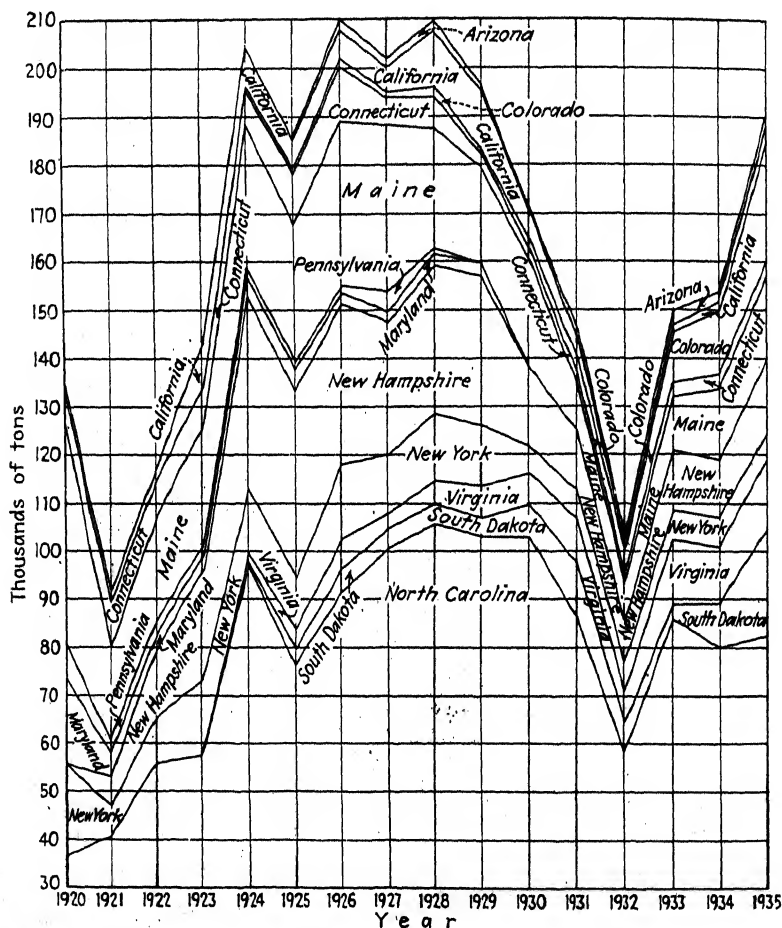


FIG. 1.—CRUDE FELDSPAR SOLD OR USED BY PRODUCERS IN THE UNITED STATES.

Another deleterious impurity is manganese, which frequently is found as dendrite on the cleavage planes of partially kaolinized feldspar.

Analyses of commercial feldspars of the United States and Canada are given in Table 2.

Pegmatites that are present or potential sources of feldspar are found in all the states of the Appalachian Region of the United States from Georgia to New York, and in the New England States. Recently Minnesota, Colorado and South Dakota have become important produc-



ing states. Other western states that are sources of feldspar are California, Nevada, Arizona, New Mexico and Texas. For years Maryland and Pennsylvania were the principal producing states. Maine took the lead in 1913, to lose it to North Carolina in 1916. Connecticut and New York have been consistent producers of 10,000 to 20,000 tons each annually for many years. For the last 10 years North Carolina has averaged about 50 per cent of the total production of the United States. During this same decade Colorado and South Dakota have come up from less than 1000 to 20,000 tons each annually. Production of crude feldspar from 1920 to 1935 is shown in Fig. 1.

Pegmatites containing commercial feldspar are found in the provinces of Canada from Nova Scotia and Labrador to Manitoba, and through the Rocky Mountain area. Most of the Province of Quebec north of the St. Lawrence and the major portion of Ontario consist of crystalline rocks containing many pegmatite dikes. The Scandinavian peninsula has long been the source of most of the feldspar used by European potteries. Andersen<sup>4</sup> reports the examination of specimens of feldspar from upwards of three hundred localities, for the most part situated in southern Norway. Pegmatite dikes are almost equally numerous in Sweden and most productive deposits have been found near Kolsva, Margritelund and Dröm. Pegmatite dikes from which feldspar is or may be obtained are also found in Czechoslovakia, Germany, France, Italy, Rumania, Russia, China, Finland, India, Japan, Australia, Egypt, South Africa and Argentina. No pegmatites that will serve as commercial sources of feldspar are known in the British Isles, but in Cornwall, near St. Austell, large deposits of semikaolinized granite or alaskite are found, from which the product known as Cornwall stone or "china stone" is obtained. A somewhat similar formation is mined at St. Yrieix, France, southwest of Limoges. What would be considered in America a very low-grade pegmatite is mined in Germany for some of the feldspathic material used in that country.

#### POLITICAL AND COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

Owing to the wide distribution of deposits over the world and the comparatively low unit value of the product, feldspar has never entered largely into world commerce. The first porcelain products in which feldspar was responsible for the fluxing action, and for which it is principally used today, were no doubt made from "natural" pottery clays containing the requisite feldspar content. During the Ting dynasty (A.D. 621-945) there is evidence of the first use of feldspar as a separate material for manufacture of vitrified products in China, but it was not until 1709 that porcelain was made in Europe.\* In that year Boettcher, at

\* C. F. Binns in *The Americana*, The Americana Co., New York, N. Y.

Meissen, Saxony, probably used feldspar in his product. The Ytterby feldspar mine in Sweden is said to have been opened in 1780 and was still reported in operation in 1925.<sup>36</sup>

The most important world movements of feldspar have been as follows: Sweden to European countries, principally Germany, France, Great Britain and Belgium; Norway to European countries, principally Germany, France, Great Britain, and Poland; Czechoslovakia to Germany, Austria, Rumania, and Poland; and Canada to the United States.

*Tariffs.*—The tariff in the United States prior to 1922 on ground feldspar imported was 20 per cent, ad valorem. This was raised to 30 per cent in 1922. No change was made in 1930. Crude feldspar was placed on duty list in 1930 at \$1 per ton of 2240 lb. This was reduced by order of the President in 1931 to \$0.50 per long ton. In Canada crude and ground feldspar entered duty free until May 1930, when a duty of 15 per cent ad valorem was applied to ground spar. This was increased to 30 per cent in 1931.

*Production and Consumption.*—Feldspar production in the United States dates back to the eighteen sixties, following shortly after the establishment of the pottery industry here.\* Between 1880 and 1898 annual production varied between 6000 and 18,000 tons. In 1899 tonnage increased to 27,202. Most of this increase was due to the new use of feldspar in scouring soap. In 1903, production was 41,891 tons; in 1911 it was 92,700 tons; and in 1924 it had increased to 204,772 tons.

Consumption in short tons may be taken very nearly at the same figures as the long tons reported for crude production, the difference of 240 lb. representing approximately the sum of the handling and other losses between crude and ground product. There are also annual differences in accord with the difference in crude inventory at the various mines and plants from year to year. Salient events affecting consumption of feldspar in the United States have been:

1. Beginning of the pottery industry about 1853.
2. First use of feldspar for artificial teeth, in 1883.
3. Discovery in 1896 that alumina is a valuable constituent in glass. (This use developed very slowly, only 1 per cent in 1913.)
4. Discovery of advantage of feldspar as base for scouring soaps, about 1897.
5. Use of considerable quantities of feldspar for poultry grit and roofing granules, which began about 1900. This use reached a peak of

\* Partly kaolinized feldspar, according to some early records, was mined by the Indians in North Carolina and shipped to England for pottery manufacture as early as 1744. Statistical records are available from the year 1880, but commercial production began at least 15 years earlier, as a mill for grinding flint and feldspar was built at Trenton, N. J., in 1865. In 1883 six states produced a total of 14,000 tons, all of which was used in pottery except a small quantity of high-grade material from Delaware used in the manufacture of artificial teeth.<sup>10</sup>

20 per cent of the total feldspar production in 1920, declining to less than 1 per cent in 1935.

6. Feldspar first used as a binder in abrasive wheels in 1907.

7. During the World War period some high-potash feldspar was used in Portland cement to increase the by-product potash recovery. About the same time a few hundred tons of high-potash spar was shipped from North Carolina to a plant near Atlanta, Ga. for potash extraction by one of the patented processes.<sup>19</sup>

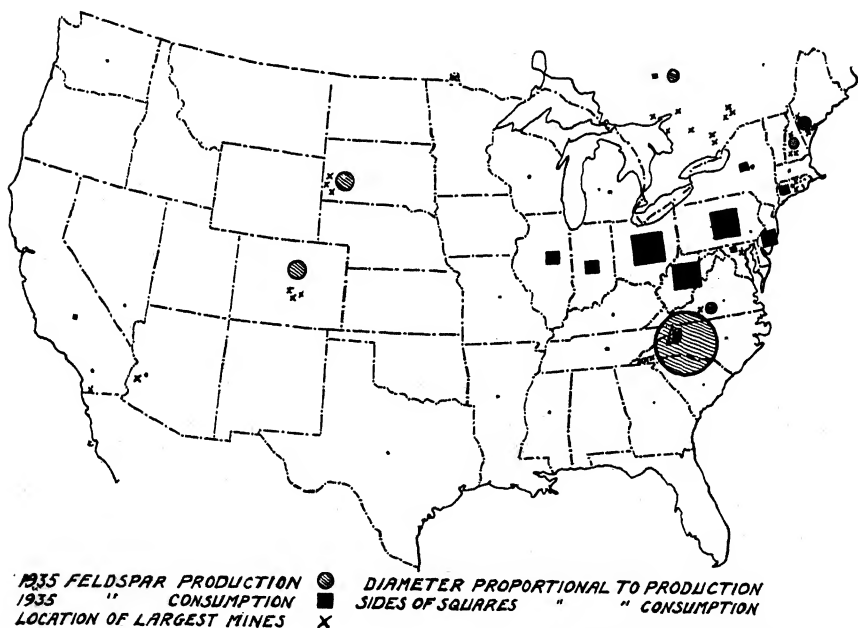


FIG. 2.—FELDSPAR PRODUCTION AND CONSUMPTION AND LOCATION OF LARGEST MINES IN UNITED STATES AND CANADA.

8. Reduction of pottery manufacture as a nonessential industry during the World War.

9. Stimulation of pottery manufacturing, especially floor and wall tile, by the building boom of 1923 to 1926.

10. Use of feldspar in container glass generally adopted by largest manufacturers in 1924.

Production was first recorded in Canada in 1890, when 700 tons of crude feldspar was shipped to the United States. The maximum Canadian production was attained in 1924 with 44,804 tons. Production dropped from 37,527 tons in 1929 to 6921 tons in 1932, and increased to 15,934 tons in 1935. Of this, 85 per cent was exported to the United States in 1924; 80 per cent in 1929; 29 per cent in 1932 and 63 per cent in 1935.

TABLE 3.—*World Production of Feldspar<sup>a</sup>*

Year	Long Tons (2240 Lb.)							Metric Tons (2205 Lb.)			
	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934
United States.....	204,772	185,706	209,989	202,497	210,811	197,699	171,788	149,480	106,396	153,051	156,663
England <sup>c</sup> .....	55,756	57,379	47,769	63,612	61,579	64,558	62,920	60,000	60,000	60,000	60,000
Sweden.....	18,999	26,321	33,434	30,152	39,290	38,475	32,739	33,113	23,693	32,567	34,468
France.....	b	b	18,951	15,000	31,500	b	b	10,700	b	b	b
Czechoslovakia <sup>d</sup> .....	b	b	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Canada.....	40,003	25,608	32,099	26,651	28,479	33,506	23,925	16,640	6,393	9,669	16,603
Norway.....	20,530	26,355	20,181	27,213	23,894	26,104	19,608	15,105	13,015	17,986	22,139
Russia.....	b	8,477	20,629	19,019	19,987	b	b	b	b	b	b
Germany.....	32,605	10,093	6,553	7,204	6,132	7,574	5,069	5,000	3,550	4,490	6,808
Italy.....	3,200	2,500	5,785	3,990	4,882	6,700	5,659	4,750	5,217	4,861	7,637
Rumania.....	b	b	1,662	1,912	2,790	2,440	1,932	3,068	681	1,309	1,026
Finland.....	659	788	800	643	700	b	b	67	1,529	2,706	3,329
Argentina.....	b	b	b	183	403	420	193	172	369	376	431
Australia.....	15	32	122	108	161	78	69	209	1,022	2,609	2,948
South America (exclusive of Argentina) <sup>e</sup> .....	b	b	99	29	29	b	b	b	b	b	6,000
Japan.....	23,050	18,743	b	b	b	b	b	b	b	b	b
Egypt.....	b	b	b	b	b	b	b	26	179	60	b
India.....	b	b	b	b	b	b	b	339	481	688	638
China.....	b	b	b	b	b	b	b	b	26,858	27,189	27,780

<sup>a</sup> Production figures for 1924-1930 from Mines Branch *Bull.* 731, Dept. of Mines, Ottawa, Canada, p. 26; for 1931-1934, U. S. Bur. Mines Minerals Yearbooks. Data for China include Manchuria, from Minerals Trade Notes, U. S. Dept. of Interior (1936) 3, No. 1.

<sup>b</sup> Data not available.

<sup>c</sup> Principally Cornwall stone.

<sup>d</sup> Estimated figures for Czechoslovakia and England 1931-1934, inclusive.

<sup>e</sup> Production for 1934 from Chile.

Table 3 shows world production of feldspar for the years 1924 to 1934, inclusive and Fig. 2 shows production and consumption in Canada and the United States, and also the locations of the largest mines.

### PROSPECTING, EXPLORATION AND MINING

Feldspar has been found outcropping plainly at the surface in so many parts of the world in reasonable proximity to consuming areas that no systematic methods have been required for prospecting and exploration. In pegmatite-bearing areas new deposits have repeatedly been found by crude methods involving for the most part only hand labor. A great deal of labor, however, if not so much money, has been wasted by the failure of prospectors and miners to use the most elementary principles of mining in opening up deposits. Watts called attention to this in 1916.<sup>40</sup>

Two or three companies have tried core drilling as a means of testing the extension of deposits. The results have not entirely justified the expenditures, because the average deposit is small and the distribution of its commercial feldspar content is extremely irregular. Exceptions are the large and comparatively uniform deposits in the western part of the United States. In most of these deposits surface indications furnish sufficient information as to size, extent and quality, so drilling is unnecessary.

There is a theory supported by a number of writers on the subject that good feldspar deposits are generally hidden by a comparatively shallow capping of mixed pegmatite material. As a result thousands of dollars have been wasted on pegmatites that a mining engineer experienced in development of feldspar would never have considered working. No better advice can be given than to work only where one finds plenty of float material or a good outcrop and to continue to work only as far as the feldspar continues. "Sticking to the ore" in the development of a mine is a maxim as old as mining itself, and it pertains to feldspar as well as to the more valuable minerals to which it is generally applied. Following this procedure, what will be the source of feldspar when all surface outcrops have been exhausted? The probability is that lower grade pegmatites still outcropping will be utilized by beneficiation methods before risks are taken to find buried deposits of the present quality.

The great majority of feldspar mines are open-cut or quarry operations and the methods used are so common to that type of operation that no description is necessary. In the United States and Canada the topography of all the mining districts is hilly or mountainous. A cut is run in or a pit sunk in good float material or mining is started directly on an outcrop. Hand drilling is done until the openings, together with surface indications, show sufficient feldspar to justify the expense of moving in a portable compressor and air drills or running a pipe line from the nearest mine.

Material is moved out by wheelbarrow, car line, sled or motor truck. It is hoisted by windlass, whim or derrick or by hoist and derrick. Discarded automobiles have been the boon of the feldspar miner. An old car obtainable for between \$10 and \$50 provides an engine suitable for hoisting, pumping or air-compressor drive. Some of these cars are suitable for haulage purposes, usually for waste disposal, and often are operated at a cost saving, even in the South where labor rates are low. At the comparatively few large feldspar-mining operations more expensive equipment is installed. Stationary power plants and railroads and aerial tramways have been built at some mines. With the advance in efficiency of the portable compressors and economy of operation of motor trucks on grades up to 20 per cent or more, it is probable no other equipment will be justified in the future even at the largest mines.

The mine of the Golding-Keene Co. at Gilsum, N. H., illustrates work on the larger type of deposits. A mica mine had been worked for many years along what was known to be the hanging wall of a large pegmatite. As exhaustion of the mica on that wall approached, it was decided to crosscut to the footwall. Almost pure feldspar was encountered for a width of about 200 ft. Ladoo<sup>28</sup> describes the development. It is interesting to record that even with the extensive exploratory workings at this deposit the effort made to project the extension of the feldspar a comparatively short distance beyond its developed limits proved in error and an inclined shaft sunk at considerable expense was abandoned after encountering only fine-grained pegmatite, from which practically no feldspar could be sorted. The operators then went back to the feldspar in the crosscuts, raised to the surface and opened out a bottle-shaped pit. This has now attained a depth of over 200 ft., is about 150 ft. wide and 300 ft. long.

The Deer Park mines comprise a group of five deposits in a horseshoe bend of the South Toe River, about three miles below Spruce Pine, N. C. No. 5, the largest, in the center of the group, is about 100 ft. wide and has been worked along the strike for a distance of 300 ft. at depths principally from 100 to 250 ft. The greater portion of the mining at Deer Park No. 5 has been done below the zone of weathering and the rock is all hard and tight. Although the workings extend almost 200 ft. below the bed of the river, there is no seepage. The main portion of the ore has been removed by room-and-pillar methods and sorted on the surface or on picking belts at the plant, one mile up the river. Where the dike forked out into the country rock, a cut and fill and a shrinkage stope were run. Hoisting is done from two different levels in Joplin-type "cans" or buckets trammed on four-wheeled trucks. Production has averaged about 1 ton of spar and 32 lb. of mica to 3 tons of waste.

Mica mentioned in the description of both of the mines is an important by-product of some feldspar operations. It is found in "wedge"

or "flat" blocks, the latter being much the more valuable of the two. Quartz is also occasionally a salable by-product.

After the deposit has been prospected, opened up and equipped for mining, the most important part of the operation is cobbing.\* A few deposits have been found containing feldspar clean enough so it could be shipped just as it is blasted from the mine, but these are exceptions. In the great majority of cases, after blasting the lumps must be broken by hand with hammers to remove quartz, mica, garnet or other minerals.

Where it is not practical to remove the quartz, grades are made containing different proportions of this mineral, but practically all mica, garnet and other minerals must be removed from all grades of crude feldspar. In mines containing both soda and potash spar, these are generally separated. A separation is also made as to soft (semikaolinized) and hard spar.

Interesting old mines still in operation in the Stockholm district in Sweden are described by Spence.<sup>35</sup>

#### PREPARATION FOR MARKET

The practice in Europe is to ship the crude spar to mills in the consuming centers, where it is ground, usually by wet methods, and used at adjacent manufacturing plants or delivered by truck to the neighboring consumers. In the United States and Canada all feldspar is ground dry. Of the 30 plants now operating in the United States, 4 are in consuming centers; 17 are at the mines and 9 are at intermediate points where milling-in-transit rates or their equivalent are enjoyed. Prior to 1916 there were a few jaw crushers in use but most of the feldspar was sledged by hand small enough to feed to chaser stones. This product was loaded in batch pebble mills and ground for a period of time that had been found necessary to reduce it to the required fineness.<sup>40</sup> Air separation, introduced in 1916, revolutionized milling methods, making possible continuous grinding.<sup>13</sup> The modernization that resulted quadrupled the grinding capacity of the industry. "Chemical control," for which a plant<sup>14</sup> was first constructed in 1926, made it possible to produce uniform grades of feldspar and relieved consumers of their most serious problem concerning raw materials. The next advance in milling came in 1930 with the production of a special granular product for the glass industry, made possible by development of high-intensity magnetic separation.<sup>15</sup>

Fig. 3 shows a detailed flowsheet of one of the two largest plants in the industry. This plant of the Tennessee Mineral Products Corporation, at Minpro, N. C., and the plant of the Consolidated Feldspar

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\* "Upon the care exercised in cobbing, sorting and grading depends the entire success of a feldspar-mining undertaking, and lack of enough knowledge or skill in these operations, or neglect to conduct them properly, must always cause trouble and invite failure." [J. L. Stuckey, former State Geologist of North Carolina in *Manufacturer's Record* (June 1927).]

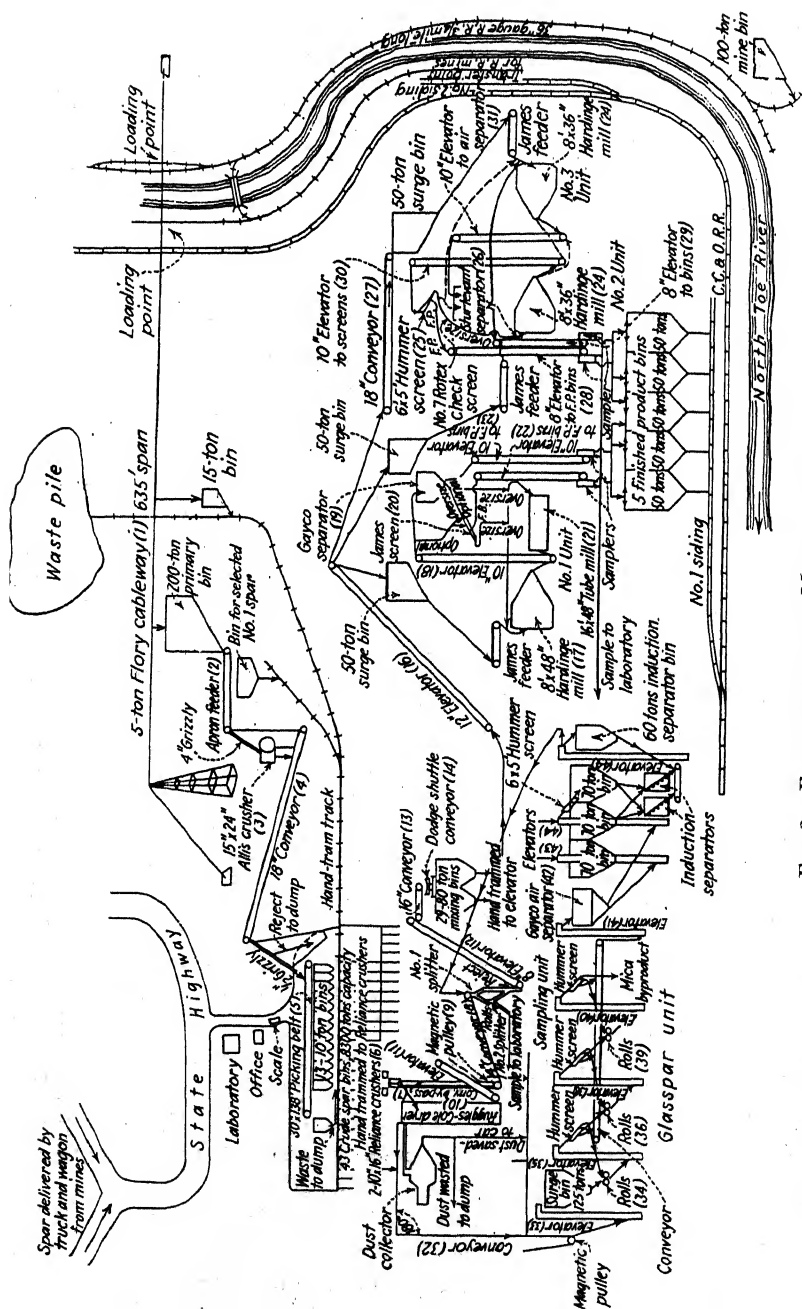


FIG. 3.—FLOWSHEET OF THE MINPRO PLANT.



Corporation at Erwin, Tenn., are the only two equipped for production of granular spar and magnetic separation. The flowsheets of the two are similar, except that the Erwin plant uses two Symons cone crushers for pulverizing in place of four sets of rolls at the Minpro plant. Some of the smaller plants produce a semigranular product by removal in part of the fines by air separation from the regular 20-mesh pebble-mill product.

Table 4 summarizes the fine-grinding equipment in the industry, July 1, 1936. It also gives the average production rates in grinding the three principal sizes, 20 mesh, 100 mesh and 200 mesh. From these and the relative consumption of these sizes, capacity of the industry has been calculated and shown in the lower portion of the table. These capacity figures may be considered excessive because they do not provide for peaks of consumption above the average that all industries must absorb. However, making 20 per cent reduction for such peaks, the total still represents more than three times the maximum consumption of ground feldspar in any year to date. Table 5 gives other production figures.

TABLE 4.—*Summary of Grinding Equipment and Capacity Based on Proportion of Different Sizes, 1931-1935*

Number of Mills	Type	Continuous or Batch	Average Size	Average Grinding Rate		
				20 Mesh	100 Mesh	200 Mesh
43	Conical.....	Continuous	8' × 48"	4.00	3.00	1.50
5	Cylindrical.....	Continuous	8' × 10'	3.50	2.50	1.30
19	Tube <sup>a</sup> .....	Continuous	5' × 22'	b	2.00	1.25
38	Cylindrical.....	Batch	7' × 6'	b	0.82	0.42

#### CALCULATED CAPACITY

Mesh	Per cent Consumed	Total Capacity, Tons	Time Ratio	Time Per cent	Average Capacity, Tons
20	47.17 <sup>c</sup>	1,234,800	29.19	37.88	467,742
100	10.81 <sup>d</sup>	1,409,760	5.85	7.59	107,001
200	42.02 <sup>e</sup>	763,992	42.02	54.53	416,605
100.00		100.00			991,348
Capacity/ two plants equipped for granular and semigranular production					86,400
Total grinding capacity/ of the industry.....					1,077,748

<sup>a</sup> A cylindrical mill with length two or more times diameter.

<sup>b</sup> Not practical for 20-mesh (coarse) grinding.

<sup>c,d,e</sup> Proportions respectively of glass, enamel and pottery feldspar.

<sup>f</sup> Capacities based on 24-hr. operation for 300 days.

The wet grinding practice in Europe until about 1920 was practically the same as has been used since the beginning of the industry. It consisted in feeding 1 to 1½-in. crushed feldspar into grinding pans or

pan mills 12 to 14 ft. in diameter, having floors of hard china stone or granite blocks. Grinding is effected by forcing through the charge of material large stones attached to radial arms. Enough water is added with the charge to make a thin sludge. After this batch is ground the required period, it is washed out through a launder to micas (a series of troughs) and thence to settling pits and storage.

Since the war, pebble mills have been introduced in a few plants. All are run wet and most as batch mills. A few conical mills are in use in closed circuit with rake or bowl classifiers. During this period a new type of classifier has been successfully used with batch mills of both the pan and cylinder type, which may be used for continuous grinding also. It is known as a "Sy-Vor" classifier and operates on the siphon-vortex principle.<sup>5</sup> These are said to be producing to specifications such as all minus 180-mesh, 16 to 17 per cent plus 600-mesh and 50 per cent minus 1000-mesh.

Magnetic separation was first used in 1930. Primarily it was introduced to remove the metallic iron resulting from the special equipment necessary to make a granular product. It was found, however, that iron-bearing minerals such as biotite, garnet, tourmaline and some muscovite were also removed. One plant in the United States is now commercially separating these minerals from run-of-mine pegmatite. A small plant in Canada is making a similar separation of nepheline syenite, producing a nepheline-feldspar product for the glass industry.

Experimental work is being actively carried on with a view to separating quartz and feldspar by froth flotation. Electrostatic separation was applied to feldspar for removal of mica in Bristol, Tenn., in 1922. Although successful, it did not appear warranted at the time. Since then it has been successfully applied to the separation of quartz and kyanite. Now, no doubt, electrostatic separation will receive attention as a method of making a quartz-feldspar separation.

In Czechoslovakia a run-of-mine pegmatite is separated by air selection and screening methods to provide a feldspar product for ceramic use. The separation of mica is effected by passing the oversize product from pebble-mill air separator through a series of burlap screens, which catch the mica and permit the feldspar to pass through. Quartz is removed by taking out of the air-separator circuit certain sizes that have been found to contain quartz segregations. A reduction of silica from 78 to 73 per cent is made.

#### TESTS AND SPECIFICATIONS

Bowles and Justice<sup>10</sup> record the first movement toward standard specifications for feldspar with the classification of grades at No. 1, No. 2 and No. 3 in 1906. However, as they say, "little progress in grading was made for many years. Most consumers designated the kind of spar they

desired simply by its geographic source." The first chemical laboratory in the industry was installed at the plant of the Tennessee Mineral Products Co. at Bristol, Tenn., in 1923. Beginning with this, serious efforts were made toward production of spar of uniform chemical composition and definitely limiting the content of impurities. This was the beginning of chemical control in the industry.<sup>23</sup>

Early in the discussion at the first meeting of the Feldspar Grinder's Institute, July 15, 1929, it was agreed that standardization of the product should be the first objective. This was accomplished through cooperation of the Bureau of Standards Division of Trade Standards and became effective Sept. 1, 1930, as Commercial Standard CS 23-30. It has been so frequently reprinted, and is so readily obtainable\* that it will not be given here. Its essential features are: (1) Physical classification based on fineness of grinding; (2) chemical classification based on composition as it influences use; (3) standard methods for making screen tests; (4) standard methods for making complete chemical analysis.

The Feldspar Code of the N.R.A. provided for standardization without reference to CS 23-30. The miners and some of the small grinders brought together under the N.R.A. refused to agree to this standardization, which to them appeared very complicated. Several attempts were made by the Code Authority to formulate a new standard. The N.R.A. went out of existence before anything was accomplished, but the Feldspar Association has continued these efforts. It has published, under date of Dec. 4, 1935, a modification of CS 23-30, which may be used by producers unable or unwilling to comply with the Commercial Standard. Principal differences are a classification based on use, rather than analysis, elimination of alkali ratio, and 3 per cent difference in grades as to silica content, instead of 2 per cent.

Disregarding the greatly improved feldspar products on the market since chemically controlled blending has become standard practice, a number of consumers have still maintained a prejudice against blending. This attitude should disappear as a result of the recent publication of the paper by Schramm and Hall.†

CS 23-30 does not give a method of fusion test, although these tests are usually made by producers and consumers. The omission was made because no method of making such tests has been found generally acceptable. Some consumers use the block test,‡ and others use the Du Bois test.<sup>20</sup> But the majority of the producers and consumers of feldspar fill

\* Superintendent of Documents, Washington, D. C. 5¢ per copy.

† Quoting from conclusion: "The results obtained lend full support to chemical control . . . In the natural intermediate feldspars we have solid solutions of one feldspar in the other and perthitic intergrowth of these solutions. Such structures are not resolved by the grinding process. It is, therefore, apparent that these mineralogical differences are without significance in the use of feldspar as a ceramic flux."<sup>24</sup>

‡ E. P. & Mfg. Co., Trenton, N. J. Pat. 1926.

a small cup or mold a cone of feldspar powder, generally using gum tragacanth or some similar organic binder, and subject this sample to the desired heat in a test or commercial kiln. The color and fusibility of such tests are only of value for comparison with other samples tested under

TABLE 5.—*Sales of Ground Feldspar*

Use	Sales, Per Cent		
	1913	1930	1935
Glass.....	1	30	49
Enamel...	9	9	9
Pottery...	76	50	37
All other <sup>a</sup> .	14	11	5

<sup>a</sup> Includes scouring compounds, roofing and cement-facing granules, poultry grit, cement manufacture (for by-product potash recovery) and abrasives. Dental porcelain (false teeth) and the use as a ceramic binder for abrasive products is included under "pottery."

TABLE 6.—*Formulas of Feldspar Products*

## PERCENTAGES

	Hotel China	Floor Tile	Wall Tile	Sheet- iron Enamel	Elec- trical Porce- lain	White- ware Glaze	Con- tainer Glass	Flat Glass
Feldspar.....	17.0	55.0	11.0	30.0	35.0	44.4	15.2	10.34
Flint.....	37.0	10.0	33.0	20.0	25.0			
Ball clay.....	20.0	15.0	27.0		20.0			
China clay.....	25.0	20.0	29.0		20.0	4.3		
Magnesium carbonate	0.5							
Whiting.....	0.5					20.4		
Borax.....				26.0				
Soda ash.....				4.0			16.2	20.74
Soda niter.....				3.0				
Fluorspar.....				3.0				
Cryolite.....				11.0				
Antimony oxide.....				3.0				
White lead.....						24.8		
Zinc oxide.....						6.1		
Sand.....							47.6	51.80
Limestone.....							18.1	15.55
Salt cake.....							0.47	1.57
Copper sulphate.....							2.43	

identical conditions. A complete chemical analysis furnishes a better guide as to the fluxing action of a feldspar than any fusion test so far devised.

Considerable microscopic work<sup>8,22,38</sup> has been done on feldspar with a view to determining more rapidly the constituents than can be done

chemically, but none are in general use. Microscopic work has also been done to determine fine particle sizes,<sup>2,39</sup> below the sizes readily obtained with the finest commercial testing sieve (325 mesh). Other methods of determining fine particle sizes are by means of the Andrews elutriator,<sup>17</sup> the sedimentation method,<sup>9</sup> and an air-analyzer method devised by Roller,<sup>32</sup> soon to be published by the American Ceramic Society.

### MARKETING, USES AND PRICE

*Marketing and Uses.*—The factors involved in the marketing of crude spar are readily determinable only in the districts where there is a competitive market for the products, as in North Carolina. However, there is a definite relation between miners wage rates and the cost of crude spar, wherever it is found. The other principal factor in the cost and marketing of crude spar is the percentage of recovery from the rock broken.

Generally speaking, it takes two man-hours to move a ton of rock in feldspar mining. Labor averages about 50 per cent of the cost. Therefore, in a district where the recovery is only 20 per cent and the wage rate 30¢ per hour, average cost of crude should be \$6 ( $5 \times 2 \times \$0.30 \times 2$ ). In another district where the recovery is 80 per cent and wage rate 50¢ per hour, crude feldspar will cost only \$2.50 per ton. Illustrations of such differences in cost and resulting marketing problems are found in the literature.<sup>43,46</sup> It is evident that if such conditions continued indefinitely the business would soon all go to the low-cost areas. That this has not happened is accounted for by other conditions such as higher transportation costs, quality differences, or rapid reduction in the percentage of recovery as the best segregated pegmatites become depleted in a new district.

With the tremendous capacity for production of ground feldspar in excess of consumption, marketing has become more a problem of selling service than of material available. As a result, the personal relations between buyer and seller are more important than large plant investment or extensive reserves of crude feldspar. The relative importance of the various markets through the last 22 years is well illustrated in Table 6.

Formulas of products in which feldspar is used vary greatly.<sup>42</sup> Those given in Table 6 are selected to show the proportion of feldspar used.

Railroad freight averages 20 to 30 per cent of the delivered cost of ground feldspar in the United States, so freight rates are an important marketing factor here. Mr. Charles Donley, Traffic Representative of the Feldspar Association, has furnished the following memorandum of the present (July 1936) basis of freight rates on feldspar in the United States:

The rates are based on a percentage of the key or base rate of first class. This so-called key or first-class rate is based on mileage and is different in the various sections of the country.

In the territory of high-density traffic, the first-class rate is lower per mile of railroad than in low-traffic density territory. The feldspar rail freight key rate is higher per mile of railroad from North Carolina to New Jersey than it is from Maine to New Jersey. The present rail freight rate from North Carolina to New Jersey or Ohio, as illustrative, is based upon 16 per cent of the key (first-class) rate while from Maine to New Jersey or Ohio the rates are based upon 21 per cent of first class. First class is a base of 100 per cent and feldspar, as the territory runs, is assessed 16 or 21 per cent of the 100 per cent rate.

West of the Mississippi, the present rail freight rates are much lower per mile of railroad than in the East. Some rates in the West, when reduced to the mileage basis are as low as 11.5 per cent of first class.

In the past, Cornwall stone and similar semikaolinized feldspathic materials have been the only products that have seriously replaced feldspar. More recently talc has been substituted for some of the feldspar in semivitreous pottery and tile. Now nepheline syenite is being introduced as a source of alumina in glass, replacing feldspar. Clay, kyanite and pyrophyllite have been tested with a view to similar use.

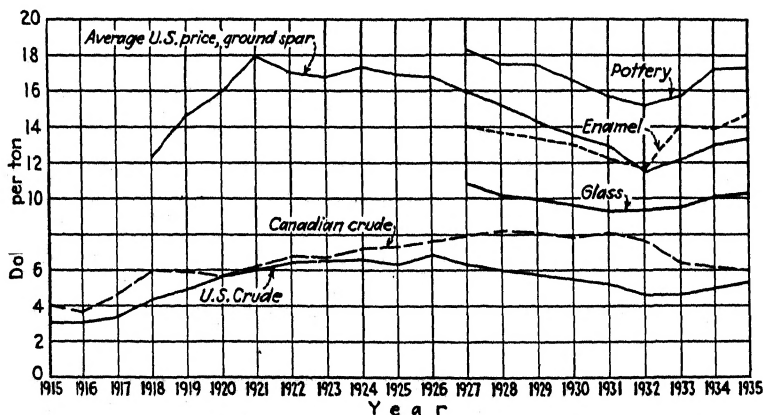


FIG. 4.—AVERAGE VALUE OF CRUDE SPAR SOLD TO GRINDERS, AND SELLING PRICE OF GROUND SPAR.

It appears improbable that any of the substitutes for feldspar so far used or considered would make serious inroads into its established markets as the principal ceramic flux and source of alumina in glass. Expansion of the feldspar market is dependent upon increased manufacture of the principal products in which it is used, pottery, enamel and glass, increased use of these products, and new uses. Pottery and enamel manufacture follow closely the trend of building construction. Flat glass follows the same trend. Container glass climbed to a new peak following "repeal." There is a suggestion of possible increased use of feldspar in pottery through colloidal preparation of slip. Educational work in the glass industry is tending toward appreciation of value of alumina content in flat as well as container glass and increase of alumina in both. If the maximum alumina now thought desirable is attained, it will double the